Stille Coupling Reactions in the Preparation of Substituted Trienic Systems

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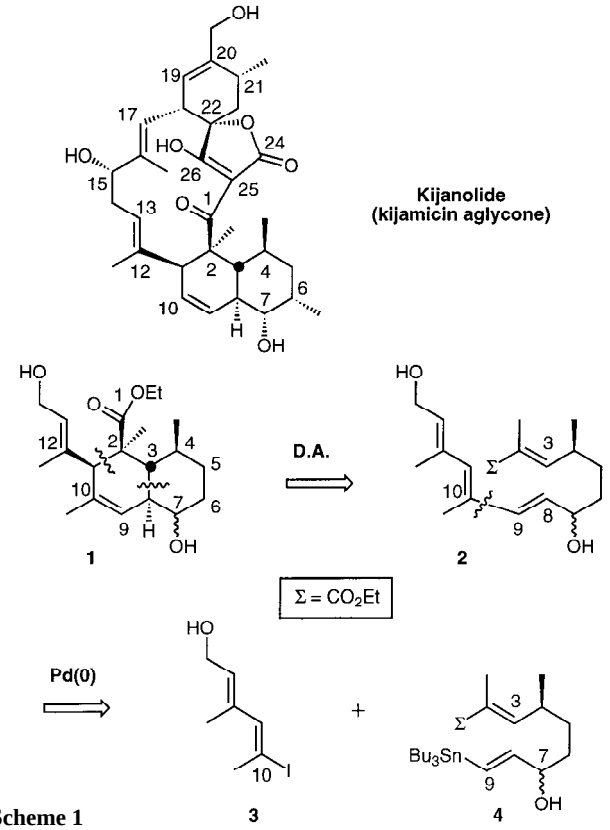
Abstract: The formation of the tetraenoate **2** was envisaged during a synthetic approach to the decalin system **1**. The iododiene **3** was obtained in high yield from the corresponding stannyl derivative. The right hand fragment **13a** was synthesized from propionate **8** using, during this sequence, a condensation of (*E*)-1-lithio-2-tributylstannylethene with aldehyde **10**. The Pd(0)-catalyzed Stille coupling reaction between **3** and **13a** was then realized in 75% yield to deliver the expected triene **23** which was then transformed into the expected tetraenoate **2**.

Key words: Stille coupling reaction, Pd(0)-catalyzed hydrostannylation, stannylcupration, (*E*)-lithio-2-tributylstannylethene

Total synthesis of the macrocyclic antibiotics chlorothricine, tetrocarcine and kijamicin (Scheme 1)[1] have been reported in the literature since 1986.[1,2] Due to their biological interest[3] and their particular structures, work in this field remained important.[4]

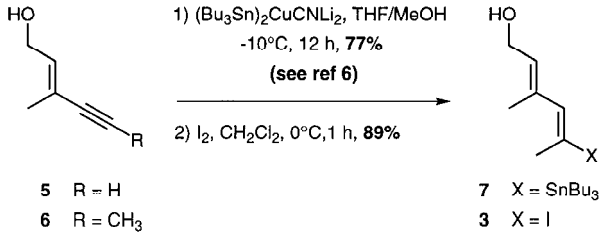
During a screening program, a new macrocyclic derivative which presents some interesting antibiotic properties, was isolated. Spectroscopic data did not give us at this time the complete structure of this new compound but its bottom half was tentatively assigned to be analogous to the tetrocarcine and kijamicin ones. Therefore the preparation of **1** was undertaken, as depicted in Scheme 1, in order to corroborate this new structure.



Scheme 1

The strategy we wanted to develop for an approach to the bottom part **1** was based on an intramolecular Diels–Alder reaction[5] performed on the tetraenoate **2** while its preparation was envisaged via a Pd(0)-catalyzed Stille coupling reaction between iododiene **3** and stannyl derivative **4**.

In a preceding work,[6] we described an efficient preparation of the stannyldiene **7**. Methylation of commercial enynol **5** gave **6** which was treated with the homocuprate $(Bu_3Sn)_2CuCNLi_2$[7] in THF/MeOH (2:1) at –10°C for 12 hours to deliver the dienylstannane **7** in 77% yield as the only stereomer (Scheme 2). A halogen-metal exchange[8] then furnished the expected iodo compound **3** in 89% yield.

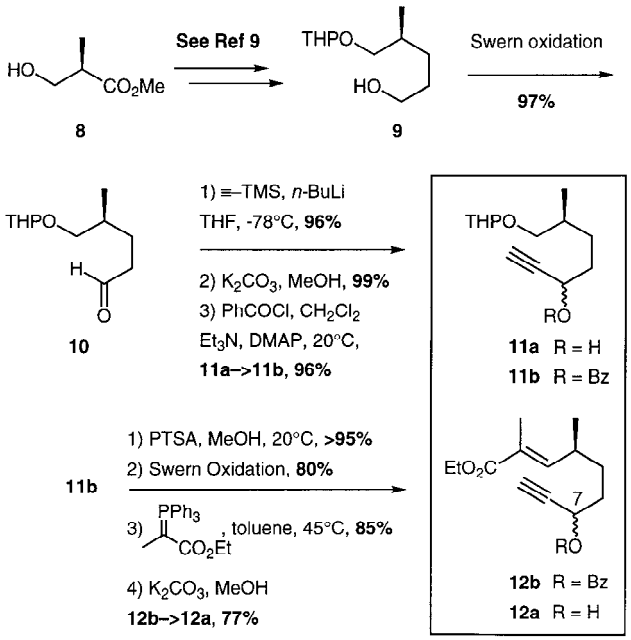


Scheme 2

The diol derivative **9** was obtained from the commercial methyl propionate **8**, as described,[9] in 74% overall yield for six steps (Scheme 3). Swern oxidation of the primary alcohol **9** led to the expected aldehyde **10** in 97% yield. After reaction of lithium trimethylsilylacetylide with aldehyde **10** (96% yield), a basic treatment (K_2CO_3, MeOH) furnished the propargyl derivative **11a** as a 1:1 mixture (99% yield) of two diastereomers at C-7. The corresponding benzoate derivative **11b** was prepared by esterification of **11a**. The unsaturated ethyl esters **12a** and **12b** were then obtained in respectively 50% and 63% overall yields from **11b**.

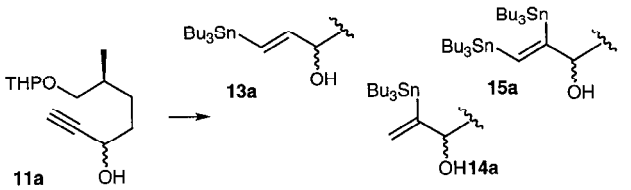
At this stage, the synthesis of the corresponding vinylstannanes **13a** and **16a,b** was attempted using either stannylcupration[10] or Pd(0)-catalyzed hydrostannylation reactions.[11,12] Pd(0)-catalyzed reaction of the propargylic alcohol **11a** was carried out in 72% yield and the distal and proximal stannyl isomers **13a** and **14a** were obtained in a 80:20 ratio (Entry 1, Table 1).

Under stannylcupration conditions [$(Bu_3Sn)_2CuCNLi_2$, THF, –40°C to –30°C, 2 h] reaction of **11a** gave a 19:25:56 mixture of the two regioisomers **13a** and **14a** and the *bis*-stannyl derivative **15a** (Entry 2, Table 1) in 86% yield. Formation of the latter compound could result from a reductive elimination of the stannylcuprate intermediate; a stabilization of the cuprate by the oxygen function of the side chain could be involved, the Cu atom reacting



Scheme 3

Table 1. Stannylation Reactions of Propargyl Derivative **11a**



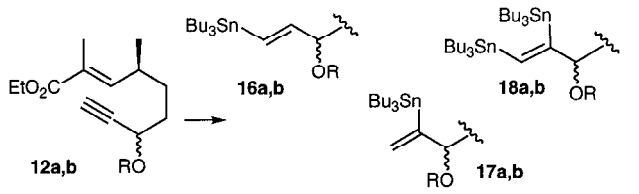
Entry	Method	Reaction Conditions	Product Ratio			Yield[a]
			13a	**14a**	**15a**	(%)
1	A	$Bu_3SnH/(Ph_3P)_2PdCl_2$/ THF, 20°C	80	20	0	72
2	B	$(Bu_3Sn)_2CuCNLi_2$/THF, –40 to –30°C, 2 h	19	25	56	86
3	C	$(Bu_3Sn)_2CuCNLi_2$/THF/ MeOH, –40 to –30°C, 2 h	63	37	0	61
4	C	$(Bu_3Sn)_2CuCNLi_2$/THF/ MeOH, 0°C, 2 h	75	25	0	81

[a] Yields refer to purified products after column chromatography on silica gel.

then as a transition metal.[12] Nevertheless this reaction could be inhibited when the stannylcupration reaction was performed in a 2:1 mixture of THF/MeOH (methanol was used in this case as a proton source to trap the stannylcuprate intermediate). The best result under these conditions was the formation of the two distal and proximal isomers **13a** and **14a** in a 75:25 ratio and 81% yield when **11a** was reacted at 0˚C (Entries 3,4, Table 1).

When the Pd(0)-catalyzed hydrostannylation was performed on the unsaturated esters **12a**, only distal stannyl derivative **16a** was obtained but in poor yield (34%, Entry 1, Table 2). However,the reaction with the benzoate derivative **12b** gave a better yield (57%) but the two regioisomers **16b** and **17b** were obtained in 60:40 ratio (Entry 4,

Table 2. Stannylation Reactions of Propargyl Derivatives **12**



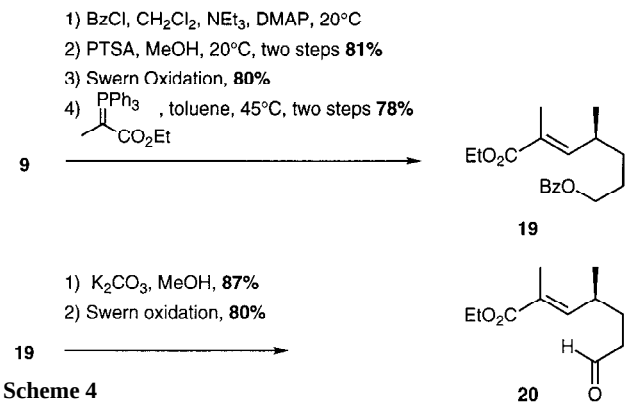
Entry	R	Method	Reaction Conditions	Product Ratio			Yield[a]
				16	**17**	**18**	(%)
1	H	A	$BuSnH/(Ph_3P)_2PdCl_2$/ THF, 20°C	100	0	0	34
2	H	B	$(Bu_3Sn)_2CuCNLi_2$/THF –40 to –30°C, 2 h	0	20	80	38
3	H	C	$(Bu_3Sn)_2CuCNLi_2$/THF/ MeOH, –40 to –30°C, 2 h	75	25	0	46
4	Bz	A	$Bu_3SnH/(Ph_3P)_2PdCl_2$/ THF, 20°C	60	40	0	57
5	Bz	C	$(Bu_3Sn)_2CuCNLi_2$/THF/ MeOH, –40 to –30°C, 2 h	100	0	0	37

[a] Yields refer to purified products after column chromatography on silica gel.

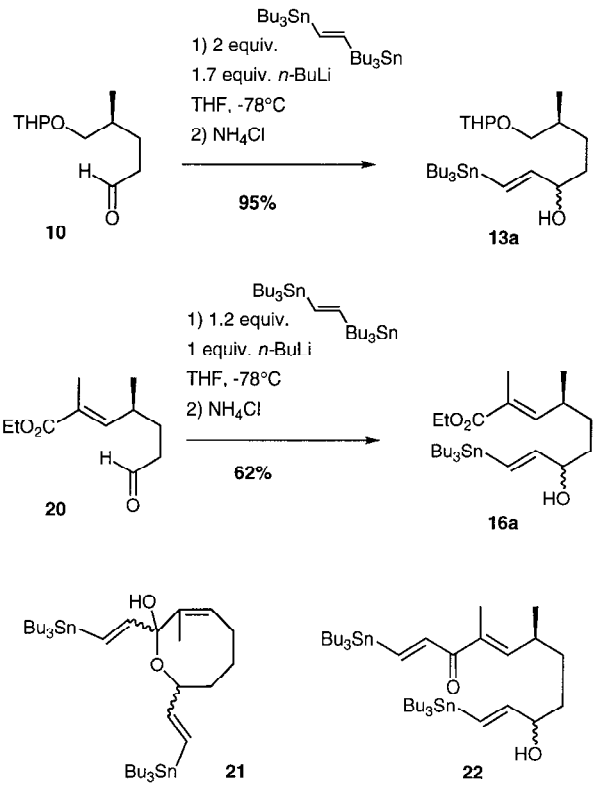
Table 2). Stannylcupration of **12a** using $(Bu_3Sn)_2$-$CuCNLi_2$ in THF also led to the formation of a bis(stannyl) compound **18a** (Entry 2, Table 2), whereas in the presence of methanol, the reaction led to a 75:25 mixture of **16a** and **17a** (46% yield, Entry 3, Table 2). When these conditions were applied to ester **12b**, only **16b** was isolated in 37% yield (Entry 5, Table 2).

As these stannylation reactions appeared to run in fair to modest yields to deliver the expected vinylstannanes **13a** or **16a,b**, we decided to generate them directly by reaction of the (*E*)-1-lithio-2-tributylstannylethene[13] with the corresponding aldehydes **10** and **20.** The aldehyde **20** was prepared from **9** in five steps and 45% overall yield as depicted in Scheme 4.

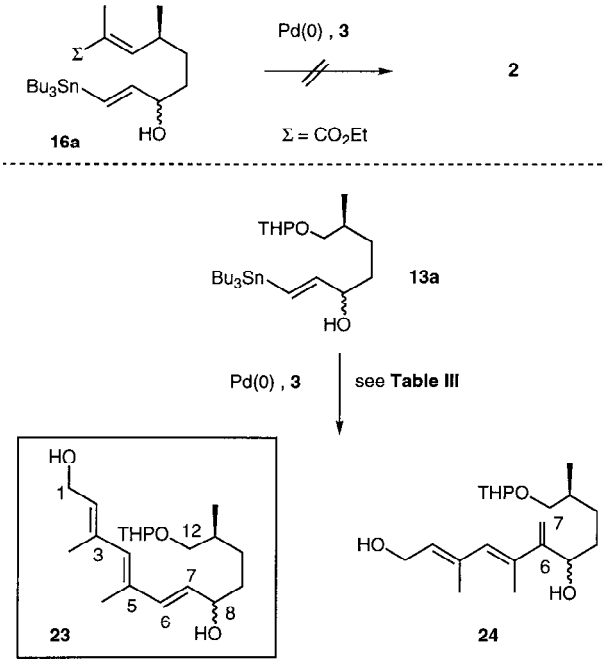
When aldehyde **10** was reacted with 1.7 equivalents of the (*E*)-1-lithio-2-tributylstannylethene [prepared by the addition of 1.7 equivalents of BuLi to 2 equivalents of the (*E*)-1,2-bis(tributylstannyl)ethene[14]], the expected pure (*E*)-vinylstannane **13a** was obtained in 95% yield (Scheme 5).



Scheme 4



Scheme 5



Scheme 6

However, using the same conditions, treatment of the aldehyde **20** led to a mixture of **16a** (40%), **21** (9%), and **22** (7%). Compounds **21** and **22** resulted in a second addition-substitution of the (*E*)-1-lithio-2-tributylstannylethene onto the carbonyl ester function. Using 1.2 equivalents of the (*E*)-1,2-bis(tributylstannyl)ethene and 1 equivalent of BuLi, **16a** was obtained as the only product in 62% yield (Scheme 5).

Having resolved the stereospecific preparation of the vinylstannyl compounds **13a** and **16a** and iodo derivative **3**, we then turned our efforts to the Stille coupling reaction.[15] This coupling reaction was first realized with $Pd(PPh_3)_4$, prepared as described by Hegedus,[16] and triene **23** was obtained in 30% yield as the best result when DMF was used as solvent instead of THF (Scheme 6 and Entries 1–3, Table 3). Under the same conditions, coupling reaction between **16a** and **3** did not work and tetraenoate **2** was not isolated.

The Stille reaction was also tested using $Pd_2(dba)_3/Ph_3P$ and CuI[17] for coupling **13a** and **3** in DMF (Entries 4,5, Table 3) but no change for the formation of **23** (20 to 34% yield) and no "copper effect" were observed in this case.

As described by Farina[18] we also tried to use tri(2-furyl)phosphine as palladium ligand but no rate acceleration was observed and triene **23** was prepared in a range of 18–26% yield (Entries 6–9, Table 3). However, counterpart using triphenylarsine and CuI in DMF at 20°C, the reaction gave a 60:40 mixture of isomeric trienes **23** and **24** in 74% yield (Entries 10,11, Table 3).

Table 3. Coupling Reactions Between **13a** and **3**

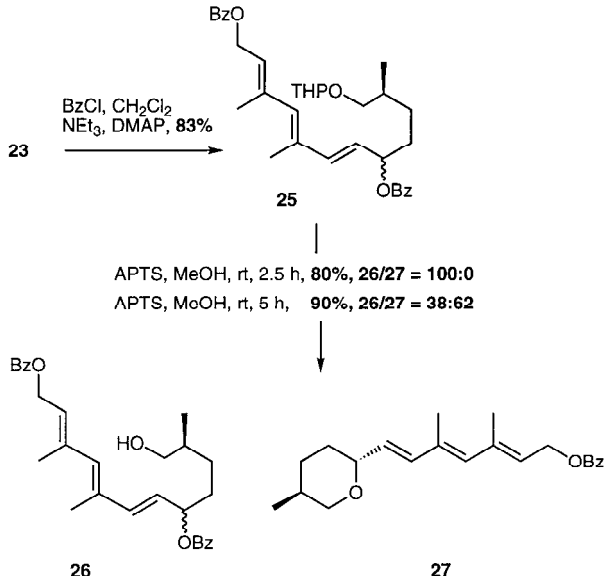
Entry	Pd(O)-Catalyst	Reaction Conditions			Product Ratio	Yield[a]
		Solvent	Time (h)	Temp (°C)	**23**/**24**	(%)
1	$(Ph_3P)_4Pd$[b]	THF	12	20	–	–
2		THF	12	reflux	–	–
3		DMF	12	20	100:0	32
4	$(dba)_3Pd_2/Ph_3P/CuI$[c]	DMF	12	20	100:0	34
5		DMF	12	40	100:0	20
6	$(dba)_3Pd_2/(2\text{-furyl})_3P/CuI$[c]	DMF	12	20	100:0	26
7		DMF	12	40	100:0	22
8		NMP	12	20	100:0	21
9		NMP	12	40	100:0	18
10	$(dba)_3Pd_2/Ph_3As/CuI$[c]	DMF	12	20	60:40	74
11		NMP	12	20	75:25	37
12	$(MeCN)_2PdCl_2$[d]	DMF	36	20	100:0	75

[a] Yields refer to purified products after column chromatography on silica gel.
[b] Prepared as described by Hegedus[16] and used in 10 mol%.
[c] Pd(0) = 5 mol%, ligand = 20 mol%, CuI = 10 mol%.
[d] Commercially available catalyst was used in 12 mol% (see Ref. 22 for typical procedures).

Formation of an "abnormal" Stille coupling product such as **24** was first described by Busacca and co-workers,[19] and involves a Heck mechanism and a palladium carbene intermediate. It was interesting to note that formation of such abnormal coupling was observed only when triphenylarsine was used as the palladium ligand. As a last attempt when $PdCl_2(MeCN)_2$ was used in DMF at 20°C (Entry 12, Table 3), the cross-coupling reaction furnished the expected triene **23** as a pure isomer in 75% yield; no trace of compound **24** was detected.

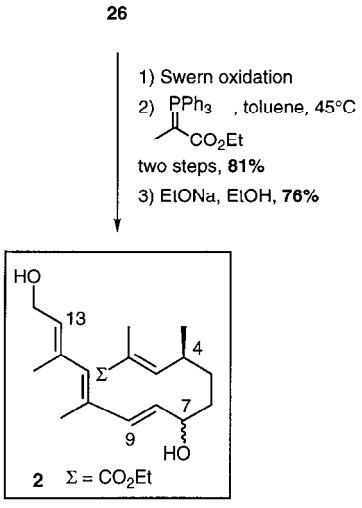
Final preparation of tetraenoate **2** was executed from the triene **23.** After protection of the two alcohol functions by esterification (BzCl, CH_2Cl_2, Et_3N, DMAP), the diben-

zoate **25** was treated under acidic conditions (TsOH, MeOH) to remove the THP group (Scheme 7). At ambient temperature reaction led to the expected alcohol **26** in 80% yield after 2.5 hours. As an interesting result, when the same reaction was performed during 5 hours, compounds **26** and **27** (single diastereomer) were obtained in 90% yield and in a 38:62 ratio .



Scheme 7

Oxidation of the primary alcohol **26** using Swern conditions led to the corresponding aldehyde which was submitted to a Wittig reaction. Removal of the benzoate functions (EtONa, EtOH, 20°C) then delivered the expected tetraenoate **2** in a 32% overall yield from **23** (43% yield for the three steps, Scheme 8).



Scheme 8

In conclusion, we were able to prepare, in a stereoselective way, iododiene **3** and vinylstannane **11a**, in 62 and 68% yield, respectively. The Stille coupling reaction between **3** and **11a** gave the expected triene **23** and the anomalous coupling product **24** using $Pd_2(dba)_3/AsPh_3$/CuI/DMF (74% yield, **23**/**24** = 60:40). Pure triene **23** was obtained in 75% yield when $PdCl_2(MeCN)_2$/DMF conditions were employed. Tetraenoate **2** was finally prepared in 15 steps from the commercial derivative **8** in 20% overall yield.

Compound **2** is now ready for the intramolecular Diels–Alder reaction envisaged for the preparation of the southern part of **1**. Work in this area is in progress.

All air and/or water sensitive reactions were carried out under argon atmosphere with anhydrous, freshly distilled solvents using standard syringe-cannula/septa techniques. THF and Et_2O were distilled from sodium/benzophenone and MeOH from $Mg(OMe)_2$. All glasswares were oven dried (110°C) and/or carefully dried with a flameless heat gun, unless otherwise stated. Petroleum ether used refers to the fraction with bp 50°C.

^1H NMR spectra were recorded in $CDCl_3$ on a Bruker WP 200 (200 MHz) or on a Bruker AM 400 (400 MHz) instrument. The chemical shifts are expressed in parts per million (ppm) referenced to residual $CHCl_3$ (δ = 7.27). Data are reported as follows: δ, chemical shift; multiplicity (recorded as s, singlet; d, doublet; t, triplet; q, quadruplet and m, multiplet), coupling constants (*J* in Hertz, Hz), integration and assignment. H,H-COSY and H,H-NOESY experiments were routinely carried out to ascertain H-H connections and configuration assignments, respectively. ^{13}C NMR spectra were recorded on the same instruments at 50.3 MHz and 100.6 MHz, respectively. ^{13}C NMR chemical shifts are expressed in parts per million (ppm), reported from the central peak of $CDCl_3$ (δ = 77.14). J-modulated spin-echo technique (J-mod) experiments were used for evaluating CH multiplicities. For Sn - ^1H or Sn - ^{13}C coupling constants the central signal is normally associated with two close pairs of satellites corresponding to both ^{117}Sn (7.5%) and ^{119}Sn (8.6%) isotopes. When detected for large coupling constants (250–300 Hz), the two different coupling constants are reported whereas in other cases (generally for small ones, < 100 Hz) average values are reported. Mass spectra were obtained on a Hewlett-Packard HP 5989B spectrometer via either direct introduction (chemical ionization, CI, NH_3) or GC/MS coupling with a Hewlett-Packard HP 5890 chromatograph. Infrared spectra were obtained on a Perkin-Elmer FT 1600 instrument using NaCl salt plates (film). Microanalyses were performed by the Service de Microanalyse, Institut de Chimie des Substances Naturelles, C.N.R.S., F-91198, Gif sur Yvette. Flash chromatography was performed on E. Merck silica gel Si 60 (40–63 mm).

(2*E*,4*E*)-5-Iodo-3-methylhexa-2,4-dien-1-ol (3):

To a solution of vinylstannane **7** (202 mg, 0.503 mmol) in CH_2Cl_2 (1 mL) at 0°C was slowly added a solution of I_2 (134 mg, 0.528 mmol) in CH_2Cl_2 (1.5 mL). After 15 min the solvent was removed under pressure and the residue was taken up in a mixture of Et_2O (2 mL), aq 1 M KF solution (1.4 mL, 1.40 mmol) and satd aq $Na_2S_2O_3$ solution (5 mL). After stirring for 3 h at r.t., the solution was filtered on a pad of Celite. The organic layer was decanted, dried ($MgSO_4$) and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 50:50) gave **3** (107 mg, 89.9%) as a pale yellow colorless oil (Chromatography must be effected quickly due to the great instability of **3**).

^1H NMR (400 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, CH_3-3), 2.06 (br s, 1 H, OH), 2.56 (d, 3 H, *J* = 1.4 Hz, CH_3, H_3-6), 4.18 (dq, 2 H, *J* = 6.7, 1.5 Hz, H_2-1), 5.49 (t, 1 H, *J* = 6.7 Hz, H-2), 6.62 (s, 1 H, H-4).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.6 (CH_3-3), 29.6 (CH_3, C-6), 59.2 (C-1), 97.6 (C-5), 129.6 (C-2), 135.4 (C-3), 143.7 (C-4).

IR (film): ν = 3332, 2954, 2918, 2869, 2853, 1651, 1615, 1434, 1377, 1066, 1000, 879, 679 cm^{-1}.

MS (DI, CI, NH_3): *m/z* = 256 ($MH^+ + NH_3$), 238 ($MH^+ + NH_3 - H_2O$), 221, 175, 128, 111, 94.

(4*S*)-4-Methyl-5-[(tetrahydropyran)-2-yloxy]pentan-1-ol (9):
To a solution of commercial methyl (*R*)-(–)-*β*-hydroxyisobutyrate (**8**; 10.0 g, 84.7 mmol) in Et_2O (90 mL) and 3,4-dihydro-2*H*-pyran (9.3 mL, 101.6 mmol, 1.2 equiv) at 0 °C was added TsOH (177 mg, 0.93 mmol, 0.01 equiv). The cold bath was removed and the mixture left to stand overnight at r.t. The mixture was then diluted with Et_2O and the organic layer was washed with satd aq $NaHCO_3$ solution, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 20:80) gave methyl (2*R*)-2-methyl-3-[(tetrahydropyran)-2-yloxy]-propanoate (16.8 g, 98%) as a colorless oil.
^{1}H NMR (400 Hz, $CDCl_3$), *two diastereomers*: δ = 1.18 (d, 1.5 H, *J* = 7.5 Hz, CH_3-2), 1.19 (d, 1.5 H, *J* = 7.0 Hz, CH_3-2), 1.45–1.62 (m, 4 H, Hb-3' + Hb-4' + H_2-5'), 1.63–1.71 (m, 1 H, Ha-3'), 1.72–1.83 (m, 1 H, Ha-4'), 2.77 (sext, 1 H, *J* = 6.8 Hz, H-2), 3.45 (dd, 0.5 H, *J* = 8.9, 5.8 Hz, Hb-3), 3.48–3.56 (m, 1 H, Hb-6'), 3.60 (t, 0.5 H, *J* = 8.1 Hz, Hb-3), 3.69 (s, 1.5 H, OCH_3), 3.70 (s, 1.5 H, OCH_3), 3.76 (t, 0.5 H, *J* = 9.7 Hz, Ha-3), 3.86–3.78 (m, 1 H, Ha-6'), 3.91 (t, 0.5 H, *J* = 9.7 Hz, Ha-3), 4.60 (t, 0.5 H, *J* = 3.1 Hz, H-2'), 4.62 (t, 0.5 H, *J* = 3.3 Hz, H-2').
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 14.0 (CH_3-2), 19.3, 19.4 (C-5'), 25.5 (C-4'), 30.5, 30.6 (C-3'), 40.2, 40.4 (C-2), 51.4 (OCH_3), 61.9, 62.1 (C-6'), 69.2, 69.4 (C-3), 98.7, 99.1 (C-2'), 173.7 (C-1).
IR (film): ν = 2945, 2875, 1742, 1455, 1262, 1124, 1078, 1060, 1034 cm^{-1}.
MS (GC, CI, NH_3): *m/z* = 220 ($MH^+ + NH_3$), 203 (MH^+), 169, 136, 119, 102, 85.

To a solution of $LiAlH_4$ (powder, 95%, 1.25 g, 31.2 mmol, 0.8 equiv) in anhyd Et_2O (80 mL) at 0 °C was added dropwise a solution of methyl (2*R*)-2-methyl-3-[(tetrahydropyran)-2-yloxy]propanoate (7.90 g, 39.1 mmol) in anhyd Et_2O (40 mL) over 30 min. The cold bath was removed and the mixture was stirred at r.t. for 3 h and cooled at 0 °C. The excess of $LiAlH_4$ was decomposed by successive addition of H_2O (1.5 mL), 15% aq NaOH solution (1.5 mL) and H_2O (4.5 mL). After 1.5 h at r.t., the mixture was filtered on a pad of Celite and the solid was washed with Et_2O. The combined filtrate and washings were dried (K_2CO_3), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 40:60 to 70:30) gave (2*R*)-2-methyl-3-[(tetrahydropyran)-2-yloxy]propan-1-ol (6.41 g, 94%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.89 (d, 1.5 H, *J* = 6.9 Hz, CH_3-2), 0.90 (d, 1.5 H, *J* = 6.9 Hz, CH_3-2), 1.48–1.63 (m, 4 H, Hb-3' + Hb-4' + H_2-5'), 1.68–1.74 (m, 2 H, Ha-3' + Ha-4'), 1.98–2.09 (m, 1 H, OH), 2.73–2.84 (m, 1 H, H-2), 3.34 (t, 0.5 H, *J* = 9.4 Hz, Hb-3), 3.47–3.83 (m, 3.5 H, 0.5 Ha-3 + Hb-3 + H_2-6'), 3.82–3.91 (m, 2 H, H_2-1), 4.57 (t, 1 H, *J* = 4.0 Hz, H-2').
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 13.5, 13.6 (CH_3-2), 19.7 (C-5'), 25.5 (C-4'), 30.7 (C-3'), 35.6, 35.8 (C-2), 62.5, 62.6 (C-6'), 67.5 (C-1), 72.2, 72.1 (C-3), 99.5, 99.2 (C-2').
IR (film): ν = 3406, 2941, 1454, 1353, 1201, 1120, 1032 cm^{-1}.
MS (GC, CI, NH_3): *m/z* = 192 ($MH^+ + NH_3$), 175 (MH^+), 108, 102, 91, 85.

Swern Oxidation: To a solution of oxalyl chloride (72 mL, 0.83 mmol, 1.2 equiv) in anhyd CH_2Cl_2 (5 mL) at –55 °C was added DMSO (128 mL, 1.65 mmol, 2.4 equiv). This was followed 5 min later with the addition via cannula of a solution of (2*R*)-2-methyl-3-[(tetrahydropyran)-2-yloxy]propan-1-ol (120 mg, 0.69 mmol) in anhyd CH_2Cl_2 (1 mL). The resulting slurry was stirred for 1 h and Et_3N (480 mL, 3.44 mmol, 5.0 equiv) was added. After 5 min, the mixture was warmed to r.t. The mixture was diluted with CH_2Cl_2 (20 mL) and washed with an ice-cold 0.5 M HCl solution (7 mL) and H_2O (7 mL). The aqueous phases were extracted with CH_2Cl_2 (20 mL). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The crude aldehyde (2*R*)-2-methyl-3-[(tetrahydropyran)-2-yloxy]propanal thus obtained was used without further purification.

IBX Oxidation: To a solution of IBX (53.2 g, 189.9 mmol, 2.2 equiv) in DMSO (400 mL) (dissolution of IBX in DMSO requires 1–1.5 h) at r.t. was added dropwise a solution of (2*R*)-2-methyl-3-[(tetrahydropyran)-2-yloxy]propan-1-ol (15.0 g, 86.3 mmol) in DMSO (100 mL). The resulting slurry was stirred for 2 h. H_2O was then added at 0 °C and the mixture was diluted with Et_2O (2 L). The organic layer was washed with H_2O (5 × 200 mL), dried ($MgSO_4$), filtered and concentrated in vacuo. The crude (2*R*)-2-methyl-3-[(tetrahydropyran)-2-yloxy]propanal thus obtained was used in the next step without further purification.
^{1}H NMR (400 Hz, $CDCl_3$), *two diastereomers*: δ = 1.13 (d, 1.5 H, *J* = 7.1 Hz, CH_3-2), 1.15 (d, 1.5 H, *J* = 7.0 Hz, CH_3-2), 1.48–1.65 (m, 4 H, Hb-3' + Ha-4' + H_2-5'), 1.65–1.75 (m, 1 H, Ha-3'), 1.75–1.85 (m, 1 H, Ha-4'), 2.61–2.72 (m, 1 H, H-2), 3.47–3.58 (m, 1 H, Hb-6'), 3.57 (t, 1 H, *J* = 9.9 Hz, Hb-3), 3.59 (t, 0.5 H, *J* = 9.9 Hz, Hb-3), 3.77–3.88 (m, 1 H, Ha-6'), 3.94 (t, 0.5 H, *J* = 10.0 Hz, Ha-3), 3.96 (dd, 0.5 H, *J* = 10.0, 9.9 Hz, Ha-3), 4.60 (t, 0.5 H, *J* = 4.3 Hz, H-2'), 4.61 (t, 0.5 H, *J* = 3.5 Hz, H-2'), 9.28 (d, 1 H, *J* = 1.9 Hz, CHO).
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 10.8 (CH_3-2), 19.3, 19.4 (C-5'), 25.5 (C-4'), 30.5 (C-3'), 46.7, 46.8 (C-2), 62.1, 62.2 (C-6'), 67.4, 67.6 (C-3), 98.8, 99.2 (C-2'), 203.7, 203.8 (C-1).
IR (film): ν = 2942, 1725, 1454, 1352, 1202, 1035 cm^{-1}.
MS (GC, CI, NH_3): *m/z* = 190 ($MH^+ + NH_3$), 173 (MH^+), 102, 85.

Horner–Emmons Reaction of Swern Oxidation's Crude Product: To a solution of NaH (powder, 80% in oil, 25 mg, 0.83 mmol, 1.2 equiv) in anhyd THF (2 mL) at 0 °C was added dropwise a solution of methyl diethylphosphonoacetate (152 μL, 0.83 mmol, 1.2 equiv) in anhyd THF (4 mL) over 5 min. The solution was stirred at r.t. for 15 min (until H_2 evolution had stopped). Then the mixture was cooled to –78 °C and a solution of the freshly prepared crude aldehyde (2*R*)-2-methyl-3-[(tetrahydropyran)-2-yloxy]propanal by Swern oxidation (see above) in anhyd THF (2 mL) was added via a cannula. After stirring for 50 min, the mixture was allowed to warm to r.t. The mixture was stirred for another 1 h and was then quenched by the addition of H_2O (5 mL). The aqueous layer was separated and extracted with Et_2O (2 × 20 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 20:80) gave methyl (2*E*,4*S*)-4-methyl-5-[(tetrahydropyran)-2-yloxy]pent-2-enoate (110 mg, 70% for two steps) as a colorless oil.

Horner–Emmons Reaction of IBX Oxidation's Crude Product: To a solution of NaH (powder, 80% in oil, 3.05 g, 101.7 mmol, 1.2 equiv) in anhyd THF (40 mL) at 0 °C was added dropwise a solution of methyl diethylphosphonoacetate (19.2 mL, 104.5 mmol, 1.2 equiv) in anhyd THF (200 mL) over 30 min. The solution was stirred at r.t. for 30 min (until H_2 evolution had stopped). Then the mixture was cooled to –78 °C and a solution of the freshly prepared crude aldehyde (2*R*)-2-methyl-3-[(tetrahydropyran)-2-yloxy]propanal by IBX oxidation (see above) in anhyd THF (160 mL) was added via a cannula. After stirring for 1.4 h, the mixture was allowed to warm to r.t. The mixture was stirred for another 1 h and was then quenched by the addition of H_2O (100 mL). The aqueous layer was separated and extracted with Et_2O (2 × 1 L). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 20:80) gave methyl (2*E*,4*S*)-4-methyl-5-[(tetrahydropyran)-2-yloxy]pent-2-enoate (17.4 g, 88% for two steps) as a colorless oil.
^{1}H MNR: (400 Hz, $CDCl_3$), *two diastereomers*: δ = 1.10 (d, 3 H, *J* = 6.8 Hz, CH_3-4), 1.48–1.63 (m, 4 H, Hb-3' + Hb-4' + H_2-5'), 1.68–1.75 (m, 1 H, Ha-3'), 1.77–1.86 (m, 1 H, Ha-4'), 2.59–2.70 (m, 1 H, H-4), 3.32 (dd, 0.5 H, *J* = 9.6, 9.5 Hz, Hb-5), 3.33 (dd, 0.5 H, *J* = 9.4, 8.9 Hz, Hb-5), 3.47–3.54 (m, 1 H, Hb-6'), 3.67 (dd, 0.5 H, *J* = 9.4, 9.0 Hz, Ha-5), 3.70 (dd, 0.5 H, *J* = 9.6, 9.5 Hz, Ha-5), 3.73 (s, 3 H, OCH_3), 3.28–3.38 (m, 1 H, Ha-6'), 4.58 (t, 0.5 H, *J* = 3.9 Hz, H-2'), 4.59 (t, 0.5 H, *J* = 3.4 Hz, H-2'), 5.87 (dd, 0.5 H, *J* = 15.6, 1.8 Hz, H-2), 5.88 (dd,

0.5 H, *J* = 15.6, 1.8 Hz, H-2), 6.96 (dd, 0.5 H, *J* = 15.8, 12.8 Hz, H-3), 6.98 (dd, 0.5 H, *J* = 15.7, 12.7 Hz, H-3).
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 16.1 (CH_3-4), 19.4 (C-5'), 25.6 (C-4'), 30.6 (C-3'), 36.7, 36.8 (C-4), 51.1 (OCH_3), 62.1, 62.2 (C-6'), 71.1, 71.2 (C-5), 98.8, 99.0 (C-2'), 120.7 (C-2), 151.4 (C-3), 166.9 (C-1).
IR (film): ν = 2948, 1726, 1659, 1436, 1273, 1122, 1039 cm^{-1}.
MS (GC, CI, NH_3): *m/z* = 246 ($MH^+ + NH_3$), 229 (MH^+), 162, 145, 102, 85.

To a solution of methyl (2*E*,4*S*)-4-methyl-5-[(tetrahydropyran)-2-yloxy]pent-2-enoate (2.11 g, 9.24 mmol) in EtOAc (30 mL) was added 5% Pd/C (1.97 g, 0.94 mmol, 0.1 equiv) and the mixture was stirred vigorously at r.t. under H_2 for 1 h. The catalyst was removed by filtration through a pad of Celite and the filtrate was concentrated in vacuo. Purification of the residue by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 20:80) gave methyl (4*S*)-4-methyl-5-[(tetrahydropyran)-2-yloxy]pentanoate (2.11 g, quantitative yield) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.90 (d, 1.5 H, *J* = 6.5 Hz, CH_3-4), 0.91 (d, 1.5 H, *J* = 6.7 Hz, CH_3-4), 1.43–1.84 (m, 9 H, H_2-3 + H-4 + H_2-3' + H_2-4' + H_2-5'), 2.28–2.42 (m, 2 H, H_2-2), 3.17 (dd, 0.5 H, *J* = 9.7, 9.6 Hz, Hb-5), 3.18 (dd, 0.5 H, *J* = 9.6, 9.4 Hz, Hb-5), 3.43–3.51 (m, 1 H, Hb-6'), 3.55 (dd, 0.5 H, *J* = 9.4, 8.8 Hz, Ha-5), 3.56 (dd, 0.5 H, *J* = 9.4, 8.7 Hz, Ha-5), 3.64 (s, 3 H, OCH_3), 3.81 (td, 1 H, *J* = 8.1, 2.8 Hz, Ha-6'), 4.52–4.57 (m, 1 H, H-2').
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 16.9 (CH_3-4), 19.6 (C-5'), 25.7 (C-4'), 29.2 (C-3), 30.8 (C-3'), 32.0 (C-2), 33.3 (C-4), 51.3 (OCH_3), 62.2 (C-6'), 72.6 (C-5), 99.1 (C-2'), 174.1 (C-1).
IR (film): ν = 2950, 1740, 1437, 1120, 1033 cm^{-1}.
MS (GC, CI, NH_3): *m/z* = 248 ($MH^+ + NH_3$), 231 (MH^+), 164, 147, 129, 115, 102, 85.

To a solution of $LiAlH_4$ (powder, 95%, 1.58 g, 39.5 mmol, 1.2 equiv) in Et_2O (40 mL) at 0 °C was added dropwise a solution of methyl (4*S*)-4-methyl-5-[(tetrahydropyran)-2-yloxy]pentanoate (7.59 g, 33.0 mmol) in Et_2O (100 mL) over 30 min. The cold bath was removed and the mixture was stirred at r.t. for 4 h and cooled at 0 °C. Then the excess of $LiAlH_4$ was decomposed by successive addition of H_2O (1 mL), 15% aq NaOH solution (1 mL) and H_2O (1.5 mL). After 1.5 h at r.t., the mixture was filtered on a pad of Celite and the solid was washed (Et_2O). The combined filtrate and washings were dried (K_2CO_3), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 50:50 to 80:20) gave (4*S*)-4-methyl-5-[(tetrahydropyran)-2-yloxy]pentan-1-ol **(9)** (6.19 g, 93%) as a colorless oil.

9:
^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.93 (d, 1.5 H, *J* = 6.7 Hz, CH_3-4), 0.95 (d, 1.5 H, *J* = 6.7 Hz, CH_3-4), 1.28–1.17 (m, 1 H, OH), 1.89–1.48 (m, 11 H, H_2-2 + H_2-3 + H-4 + H_2-3' + H_2-4' + H_2-5'), 3.20 (dd, 0.5 H, *J* = 9.4, 6.2 Hz, Hb-5), 3.25 (dd, 0.5 H, *J* = 9.6, 6.2 Hz, Hb-5), 3.79–3.48 (m, 4 H, H_2-1 + Ha-5 + Hb-6'), 3.86 (td, 1 H, *J* = 9.3, 3.6 Hz, Ha-6'), 4.58 (t, 1 H, *J* = 3.2 Hz, H-2').
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 17.0 (CH_3-4), 19.6 (C-5'), 25.6 (C-4'), 29.9 (C-3), 30.3 (C-2), 30.8 (C-3'), 33.2 (C-4), 62.2 (C-6'), 63.0 (C-1), 73.0 (C-5), 99.0 (C-2').
IR (film): ν = 3397, 2938, 1453, 1352, 1200, 1120, 1061, 1032 cm^{-1}.
MS (GC, CI, NH_3): *m/z* = 220 ($MH^+ + NH_3$), 203 (MH^+), 136, 120, 119, 102, 85.
Anal. calc. for $C_{11}H_{20}O_3$ (201.9): C, 65.31; H, 10.96; found C, 65.37; H, 11.05.

(4*S*)-4-Methyl-5-[(tetrahydropyran)-2-yloxy]pentanal (10):
To a solution of oxalyl chloride (2.6 mL, 29.7 mmol, 1.2 equiv) in CH_2Cl_2 (80 mL) at –55 °C was added DMSO (4.6 mL, 59.3 mmol, 2.4 equiv). This was followed 5 min later with the addition via cannula of a solution of the alcohol **9** (5.0 g, 24.7 mmol) in CH_2Cl_2 (40 mL). The resulting slurry was stirred for 1 h and Et_3N (17.2 mL, 123.6 mmol, 5 equiv) was added. After 5 min, the mixture was warmed to r.t. The mixture was diluted with CH_2Cl_2 (100 mL) and was washed with an ice-cold 1M HCl solution (123 mL) and H_2O (123 mL). The aqueous phases were extracted with CH_2Cl_2 (200 mL). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 20:80 to 30:70) gave the aldehyde **10** (4.75 g, 97%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.91 (d, 1.5 H, *J* = 6.7 Hz, CH_3-4), 0.92 (d, 1.5 H, *J* = 6.7 Hz, CH_3-4), 1.84–1.42 (m, 9 H, H_2-3 + H-4 + H_2-3' + H_2-4' + H_2-5'), 2.47 (td, 2 H, *J* = 6.5, 1.8 Hz, H_2-2), 3.18 (t, 0.5 H, *J* = 9.6 Hz, Hb-5), 3.19 (dd, 0.5 H, *J* = 9.6, 9.5 Hz, Hb-5), 3.52–3.44 (m, 1 H, Hb-6'), 3.56 (dd, 1 H, *J* = 9.8, 9.5 Hz, Ha-5), 3.57 (dd, 0.5 H, *J* = 10.0, 9.5 Hz, Ha-5), 3.82 (td, 1 H, *J* = 8.7, 2.1 Hz, Ha-6'), 4.53 (t, 0.5 H, *J* = 3.9 Hz, H-2'), 4.54 (t, 0.5 H, *J* = 2.9 Hz, H-2'), 9.27 (t, 1 H, *J* = 1.8 Hz, H-1).
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 17.0 (CH_3-4), 19.7 (C-5'), 25.6 (C-4'), 26.2 (C-3), 30.8 (C-3'), 33.2 (C-4), 41.7 (C-2), 62.3 (C-6'), 72.5 (C-5), 99.1, 99.2 (C-2'), 202.2 (C-1).
IR (film): ν = 2940, 1725, 1453, 1122, 1063, 1033 cm^{-1}.
MS (GC, CI, NH_3): *m/z* = 218 ($MH^+ + NH_3$), 201 (MH^+), 200, 183, 134, 116, 102, 85.
Anal. calc. for $C_{11}H_{20}O_3$ (201.9): C, 65.97; H, 10.07; found C, 65.15; H, 10.11.

(3*R/S*,6*S*)-6-Methyl-7-[(tetrahydropyran)-2-yloxy]hept-1-yn-3-ol (11a):
To a solution of commercial (trimethylsilyl)acetylene (368 mg, 3.74 mmol, 2.0 equiv) in anhyd THF (10 mL) at –78 °C was added BuLi (1.6 M solution in hexane, 1.4 mL, 2.25 mmol, 1.2 equiv). The mixture was stirred at 0 °C for 1.5 h and cooled to –78 °C. Then a solution of freshly prepared aldehyde **10** (375 mg, 1.87 mmol) in anhyd THF (2 mL) was added via cannula. After stirring for 50 min, the mixture was quenched by the addition of satd aq NH_4Cl solution. The mixture was allowed to warm to r.t. and then extracted with Et_2O (1 × 30 mL). The combined extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 40:60 to 50:50) gave (3*R/S*,6*S*)-6-methyl-7-[(tetrahydropyran)-2-yloxy]-1-(trimethylsilyl)hept-1-yn-3-ol (537 mg, 96%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$), *four diastereomers*: δ = 0.17 [s, 9 H, $Si(CH_3)_3$], 0.92 (d, 1.5 H, *J* = 6.8 Hz, CH_3-6), 0.93 (d, 1.5 H, *J* = 6.8 Hz, CH_3-6), 1.86–1.48 (m, 11 H, H_2-4 + H_2-5+ H-6 + H_2-3' + H_2-4' + H_2-5'), 2.32–2.37 (m, 1 H, OH), 3.18 (dd, 0.5 H, *J* = 10.0 Hz, 9.4 Hz, Hb-7), 3.23 (t, 0.5 H, *J* = 9.5 Hz, Hb-7), 3.48–3.54 (m, 1 H, Hb-6'), 3.58 (dd, 0.5 H, *J* = 10.8, 9.5 Hz, Ha-7), 3.59 (dd, 0.5 H, *J* = 10.6, 9.5 Hz, Ha-7), 3.85 (td, 1 H, *J* = 8.3, 2.9 Hz, Ha-6'), 4.29–4.38 (m, 1 H, H-3), 4.58 (t, 1 H, *J* = 3.9 Hz, H-2').
^{13}C NMR (50 MHz, $CDCl_3$), *four diastereomers*: δ = –0.3 [$Si(CH_3)_3$], 17.1, 17.2 (CH_3-6), 19.6 (C-5'), 25.6 (C-4'), 29.2, 29.3 (C-5), 30.8 (C-3'), 33.2 (C-6), 35.2, 35.3 (C-4), 62.2 (C-6'), 63.1 (C-3), 72.8, 72.9 (C-7), 89.2, 89.3 (C-2), 99.0, 98.9 (C-2'), 107.1 (C-1).
IR (film): ν = 3418, 2953, 2169, 1454, 1353, 1250, 1120, 1032, 843, 808, 760 cm^{-1}.
MS (GC, CI, NH_3): *m/z* = 316 ($MH^+ + NH_3$), 299 (MH^+), 281, 232, 215, 197, 102, 85.

A solution of (3*R/S*,6*S*)-6-methyl-7-[(tetrahydropyran)-2-yloxy]-1-(trimethylsilyl)hept-1-yn-3-ol (486 mg, 1.63 mmol) and anhyd K_2CO_3 (338 mg, 2.44 mmol, 1.5 equiv) in anhyd MeOH (9 mL) was stirred 1 h at r.t. Then the mixture was extracted with Et_2O and washed with H_2O and brine. The organic layer was dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 30:70) gave **11a** (368 mg, 99%) as a colorless oil.

11a:
^{1}H NMR (400 MHz, $CDCl_3$), *four diastereomers*: δ = 0.93 (d, 1.5 H, *J* = 6.2 Hz, CH_3-6), 0.94 (d, 1.5 H, *J* = 6.3 Hz, CH_3-6), 1.81–1.48 (m,

12 H, H_2-4 + H_2-5 + H-6 + H_2-3' + H_2-4' + H_2-5' + OH), 2.45 (s, 0.5 H, H-1), 2.46 (s, 0.5 H, H-1), 3.18 (dd, 0.5 H, *J* = 9.6, 9.4 Hz, Hb-7), 3.24 (dd, 0.5 H, *J* = 9.5, 9.4 Hz, Hb-7), 3.48–3.52 (m, 1 H, Hb-6'), 3.56 (dd, 0.5 H, *J* = 12.0, 9.7 Hz, Ha-7), 3.60 (dd, 0.5 H, *J* = 9.6, 9.3 Hz, Ha-7), 3.85 (td, 1 H, *J* = 7.7, 2.9 Hz, Ha-6'), 4.32–4.39 (m, 1 H, H-3), 4.57 (t, 0.5 H, *J* = 3.3 Hz, H-2'), 4.58 (t, 0.5 H, *J* = 3.3 Hz, H-2').
^{13}C NMR (50 MHz, $CDCl_3$), *four diastereomers*: δ = 17.2, 17.3 (CH_3-6), 19.6 (C-5'), 25.6 (C-4'), 29.1 (C-5), 30.7 (C-3'), 33.1, 33.2 (C-6), 35.2 (C-4), 62.2 (C-6'), 62.4, 62.5 (C-3), 76.49 (C-1), 85.2 (C-2), 99.0, 99.1 (C-2').
IR (film): ν = 3407, 3308, 2947, 2872, 2361, 1456, 1261, 1119, 1062, 1025 cm^{-1}.
MS (GC, CI, NH_3): *m/z* = 244 ($MH^+ + NH_3$), 227 (MH^+), 160, 143, 102, 85.
Anal. calc. for $C_{13}H_{22}O_3$ (226.3): C, 68.99; H, 9.80; found C, 68.84; H, 9.72.

(3*R*/*S*,6*S*)-3-(Benzoyloxy)-6-methyl-7-[(tetrahydropyran)-2-yloxy]hept-1-yne (11b):
To a solution of (3*R*/*S*,6*S*)-6-methyl-7-[(tetrahydropyran)-2-yloxy]-1-(trimethylsilyl)hept-1-yn-3-ol (see preparation of **11a**, 100 mg, 0.34 mmol) and DMAP (0.02 equiv) in anhyd CH_2Cl_2 (5 mL) at –30 °C were added Et_3N (280 µL, 2.01 mmol, 6.0 equiv) and benzoyl chloride (117 µL, 1.01 mmol, 3.0 equiv). The cold bath was removed and the mixture was stirred at 0 °C for 2 h. Then the mixture was diluted with Et_2O. The organic layer was washed with H_2O and brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 30:70) gave (3*R*/*S*,6*S*)-3-(benzoyloxy)-6-methyl-7-[(tetrahydropyran)-2-yloxy]-1-(trimethylsilyl)hept-1-yne (110 mg, 82%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$), *four diastereomers*: δ = 0.19 [s, 9 H, $Si(CH_3)_3$], 0.97 (d, 1.5 H, *J* = 6.7 Hz, CH_3-6), 0.98 (d, 1.5 H, *J* = 6.6 Hz, CH_3-6), 1.51–2.01 (m, 11 H, H_2-4 + H_2-5 + H-6 + H_2-3' + H_2-4' + H_2-5'), 3.21 (dd, 0.5 H, *J* = 10.0, 9.7 Hz, Hb-7), 3.25 (t, 0.5 H, *J* = 9.4 Hz, Hb-7), 3.47–3.53 (m, 1 H, Hb-6'), 3.58 (t, 0.5 H, *J* = 9.4 Hz, Ha-7), 3.61 (dd, 0.5 H, *J* = 9.6, 9.4 Hz, Ha-7), 3.828–3.88 (m, 1 H, Ha-6'), 4.59 (t, 1 H, *J* = 3.3 Hz, H-2'), 5.6 (t, 0.5 H, *J* = 6.3 Hz, H-3), 5.65 (t, 0.5 H, *J* = 6.3 Hz, H-3), 7.42–7.50 (m, 2 H, H-arom), 7.62–7.53 (m, 1 H, H-arom), 8.04–8.13 (m, 2 H, H-arom).
^{13}C NMR (50 MHz, $CDCl_3$), *four diastereomers*: δ = –0.05 [$(CH_3)_3Si$], 17.2 (CH_3-6), 19.4 (C-5'), 25.8 (C-4'), 29.4 (C-5), 30.9 (C-3'), 32.9 (C-4), 33.4 (C-6), 62.3 (C-6'), 65.4 (C-3), 72.9 (C-7), 90.8 (C-2), 99.1, 99.2 (C-2'), 103.3 (C-1), 128.5 (C-arom), 130.0 (C-arom), 130.7 (C-arom), 133.1 (C-arom), 165.3 [O*C*(O)Ph].
IR (film): ν = 2954, 2871, 2177, 1724, 1600, 1584, 1452, 1265, 1105, 1034, 843, 760, 712 cm^{-1}.
MS (DI, CI, NH_3): *m/z* = 420 ($MH^+ + NH_3$), 403 (MH^+), 336, 319, 214, 197, 102.

To a solution of (3*R*/*S*,6*S*)-3-(benzoyloxy)-6-methyl-7-[(tetrahydropyran)-2-yloxy]-1-(trimethylsilyl)hept-1-yne (908 mg, 2.26 mmol) in THF (10 mL) at r.t. was added in one portion TBAF•$3H_2O$ (powder, 1.42 g, 4.52 mmol, 2 equiv). The resulting mixture was stirred for 1 h at 20 °C, treated with satd aq $NaHCO_3$ solution and extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 20:80) gave **11b** (347 mg, 47%) as a colorless oil.

To a solution of **11a** (500 mg, 2.2 mmol) and DMAP (15 mg, 0.05 equiv) in anhyd CH_2Cl_2 (20 mL) at –30 °C were added Et_3N (2 mL, 13.2 mmol, 6.0 equiv) and benzoyl chloride (7.7 mL, 6.6 mmol, 3.0 equiv). The cold bath was removed and the mixture was stirred at 0 °C for 12 h. Then the mixture was diluted with Et_2O. The organic layer was washed with H_2O and brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 20:80) gave **11b** (695 mg, 96%) as a colorless oil.

11b:
^{1}H NMR (400 MHz, $CDCl_3$), *four diastereomers*: δ = 0.98 (d, 1.5 H, *J* = 6.4 Hz, CH_3-6), 0.99 (d, 1.5 H, *J* = 6.7 Hz, CH_3-6), 1.51–2.03 (m, 11 H, H_2-4 + H_2-5 + H-6 + H_2-3' + H_2-4' + H_2-5'), 2.49 (s, 0.5 H, H-1), 2.50 (s, 0.5 H, H-1), 3.23 (dd, 1 H, *J* = 9.6, 9.3 Hz, Hb-7), 3.26 (dd, 0.5 H, *J* = 9.7, 9.2 Hz, Hb-7), 3.47–3.52 (m, 1 H, Hb-6'), 3.59 (t, 0.5 H, *J* = 9.5 Hz, Ha-7), 3.63 (dd, 0.5 H, *J* = 9.6, 9.5 Hz, Ha-7), 3.83–3.88 (m, 1 H, Ha-6'), 4.59 (t, 1 H, *J* = 3.5 Hz, H-2'), 5.61 (t, 0.5 H, *J* = 6.3 Hz, H-3), 5.62 (t, 0.5 H, *J* = 6.3 Hz, H-3), 7.47 (t, 2 H, *J* = 7.5 Hz, H-arom), 7.59 (t, 1 H, *J* = 7.4 Hz, H-arom), 8.08 (d, 2 H, *J* = 8.3 Hz, H-arom).
^{13}C NMR (50 MHz, $CDCl_3$), *four diastereomers*: δ = 17.1 (CH_3-6), 19.5 (C-5'), 25.6 (C-4'), 29.1 (C-5), 30.8 (C-3'), 32.5 (C-4), 33.2 (C-6), 62.0, 62.1 (C-6'), 64.7 (C-3), 72.7 (C-7), 73.7 (C-1), 81.5 (C-2), 99.0 (C-2'), 128.4 (C-arom), 129.8 (C-arom), 133.1 (C-arom), 165.4 [O*C*(O)Ph].
IR (film): ν = 3293, 2940, 2870, 2359, 1723, 1601, 1451, 1266, 1106, 1031, 868, 814, 712 cm^{-1}.
MS (GC, CI, NH_3): *m/z* = 348 ($MH^+ + NH_3$), 331 (MH^+), 264, 247, 102, 85.
Anal. calc. for $C_{20}H_{26}O_4$ (330.4): C, 72.70; H, 7.93; found C, 72.57; H, 7.88.

Ethyl (2*E*,4*S*,7*R*/*S*)-2,4-Dimethyl-7-hydroxynon-2-en-8-ynoate (12a):
A solution of **12b** (see below, 440 mg, 1.34 mmol) and anhyd K_2CO_3 (278 mg, 2.01 mmol, 1.5 equiv) in anhyd EtOH (10 mL) was stirred at r.t. overnight. Then the mixture was extracted with Et_2O and washed with H_2O and brine. The organic layer was dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 40:60 to 50:50) gave **12a** (231 mg, 77%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.99 (d, 3 H, *J* = 6.6 Hz, CH_3-4), 1.26 (t, 3 H, *J* = 7.1 Hz, C*H*$_3$CH$_2$O), 1.41–1.67 (m, 4 H, H_2-5 + H_2-6), 1.80 (s, 3 H, CH_3-2), 2.43 (s, 0.5 H, H-9), 2.44 (s, 0.5 H, H-9), 2.44–2.52 (m, 1 H, H-4), 2.77 (d, 1 H, *J* = 5.3 Hz, OH), 4.14 (q, 2 H, *J* = 7.1 Hz, CH_3C*H*$_2$O), 4.27–4.33 (m, 1 H, H-7), 6.49 (d, 1 H, *J* = 10.1 Hz, H-3).
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 12.5 (*C*H_3CH$_2$O), 14.2 (CH_3-4), 20.0 (CH_3-2), 32.0, 32.1 (C-5), 32.9, 33.0 (C-4), 35.4 (C-6), 60.6 (CH_3*C*H_2O), 61.9, 62.0 (C-7), 72.9 (C-9), 85.0 (C-8), 126.9 (C-2), 147.3 (C-3), 168.5 [*C*(O)OEt].
IR (film): ν = 3442, 3301, 2929, 2870, 2361, 1706, 1647, 1456, 1368, 1260, 1191, 1127, 1093, 1028, 751 cm^{-1}.
MS (DI, CI, NH_3): *m/z* = 242 ($MH^+ + NH_3$), 225 (MH^+), 207, 196, 179, 161, 151, 133, 86.
Anal. calc. for $C_{13}H_{20}O_3$ (224.3): C, 69.61; H, 8.99; found C, 69.07; H, 8.94.

Ethyl (2*E*,4*S*,7*R*/*S*)-7-(Benzoyloxy)-2,4-dimethylnon-2-en-8-ynoate (12b):
To a solution of **11b** (528 mg, 1.60 mmol) in MeOH (50 mL) at r.t. was added TsOH (98 mg, 0.48 mmol, 0.3 equiv) and the mixture was stirred at r.t. for 2 h. Then it was quenched by the addition of Et_3N (134 µL, 0.96 mmol, 0.6 equiv). After 5 min the MeOH was removed under reduced pressure and the residue was taken up in CH_2Cl_2. The CH_2Cl_2 layer was washed with H_2O and the aqueous layer was separated and extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 50:50 to 80:20) gave (2*S*,5*R*/*S*)-5-(benzoyloxy)-2-methylhept-6-yn-1-ol, as a colorless oil (361 mg, 92%) .
^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.98 (d, 3 H, *J* = 6.5 Hz, CH_3-2), 1.37–1.44 (m, 2 H, H_2-3), 1.67–1.75 (m, 2 H, H-2 + OH), 1.90–2.07 (m, 2 H, H_2-4), 2.51 (s, 0.5 H, H-7), 2.52 (s, 0.5 H, H-7), 3.48–3.55 (m, 2 H, H_2-1), 5.60–5.64 (m, 1 H, H-5), 7.47 (t, 2 H, *J* = 7.7 Hz, H-arom), 7.60 (t, 1 H, *J* = 7.7 Hz, H-arom), 8.08 (d, 2 H, *J* = 7.7 Hz, H-arom).

^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 16.5 (CH_3-2), 28.5 (C-3), 32.3, 32.4 (C-4), 35.4 (C-2), 64.7 (C-5), 67.9 (C-1), 73.9, 74.0 (C-7), 81.3 (C-6), 128.4 (C-arom), 129.8 (C-arom), 129.9 (C-arom), 133.2 (C-arom), 165.6 [O*C*(O)Ph].
IR (film): ν = 3296, 2956, 2874, 2361, 1722, 1602, 1491, 1316, 1270, 1108, 1070, 1026, 712 cm^{-1}.
MS (DI, CI, NH_3): *m/z* = 264 ($MH^+ + NH_3$), 247 (MH^+), 229, 160, 142, 125, 105, 94.

To a solution of oxalyl chloride (320 µL, 3.66 mmol, 2.5 equiv) in anhyd CH_2Cl_2 (20 mL) at –55 °C was added DMSO (567 µL, 7.33 mmol, 5.0 equiv). This was followed 5 min later with the addition of a solution of (2*S*,5*R/S*)-5-(benzoyloxy)-2-methylhept-6-yn-1-ol (361 mg, 1.47 mmol) in anhyd CH_2Cl_2 (4 mL). The resulting slurry was stirred for 1 h and Et_3N (2.66 mL, 19.1 mmol, 13.0 equiv) was added. After stirring for 5 min, the mixture was warmed to r.t. The mixture was diluted with CH_2Cl_2 (40 mL) and was washed with an ice-cold 1M HCl solution (19 mL) and H_2O (19 mL). The aqueous phases were extracted with CH_2Cl_2 (40 mL), the organic layers were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The crude aldehyde (2*S*,5*R/S*)-5-(benzoyloxy)-2-methylhept-6-ynal thus obtained was used in the next step without further purification.
^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 1.17 (d, 3 H, *J* = 7.2 Hz, CH_3-2), 1.36–1.44 (m, 2 H, H_2-3), 1.95–2.04 (m, 2 H, H_2-4), 2.41–2.48 (m, 1 H, H-2), 2.52 (s, 0.5 H, H-7), 2.53 (s, 0.5 H, H-7), 5.60–5.63 (m, 1 H, H-5), 7.46 (t, 2 H, *J* = 7.7 Hz, H-arom), 7.60 (t, 1 H, *J* = 7.7 Hz, H-arom), 8.06 (d, 2 H, *J* = 7.7 Hz, H-arom), 9.65 (s, 1 H, H-1).
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 13.0 (CH_3-2), 25.3 (C-3), 31.7 (C-4), 45.3 (C-2), 63.7 (C-5), 74.2 (C-7), 80.5 (C-6), 128.2 (C-arom), 129.4 (C-arom), 133.0 (C-arom), 164.9 [O*C*(O)Ph], 203.7 (C-1).
IR (film): ν = 2933, 2360, 1721, 1451, 1316, 1266, 1177, 1107, 1070, 1025, 713 cm^{-1}.
MS (DI, CI, NH_3): *m/z* = 262 ($MH^+ + NH_3$), 245 (MH^+), 215, 123, 105, 94.

A solution of the crude aldehyde (2*S*,5*R/S*)-5-(benzoyloxy)-2-methylhept-6-ynal (520 mg, see above) and (ethoxycarbonylethylidene)triphenylphosphorane (2.23 g, 6.15 mmol, 4.2 equiv) in anhyd toluene (10 mL) was warmed at 45 °C for 8 h. Then the toluene was removed under reduced pressure. The residue was dissolved in Et_2O, filtered on a pad of Celite and the solid was washed with Et_2O. The combined filtrate and washings were concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 20:80) gave **12b** (335 mg, 69% for two steps) as a colorless oil.

12b:
^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 1.06 (d, 3 H, *J* = 6.5 Hz, CH_3-4), 1.29–1.34 (m, 3 H, CH_3CH$_2$O), 1.55–1.66 (m, 2 H, H_2-5), 1.85–1.90 (m, 5 H, H_2-6 + CH_3-2), 2.50 (s, 0.5 H, H-9), 2.51 (s, 0.5 H, H-9), 2.54–2.59 (m, 1 H, H-4), 4.22 (q, 2 H, *J* = 7.1 Hz, CH$_3$CH_2O), 5.58–5.62 (m, 1 H, H-7), 6.55 (br d, 1 H, *J* = 9.9 Hz, H-3), 7.47 (t, 2 H, *J* = 7.7 Hz, H-arom), 7.60 (t, 1 H, *J* = 7.7 Hz, H-arom), 8.07 (d, 2 H, *J* = 7.6 Hz, H-arom).
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 12.5 (*C*H$_3$CH$_2$O), 14.3 (CH_3-4), 19.9 (CH_3-2), 32.1 (C-6), 32.8 (C-5), 32.9 (C-4), 60.4 (CH$_3$*C*H$_2$O), 64.3 (C-7), 74.0 (C-9), 81.1 (C-8), 127.3 (C-2), 128.7 (C-arom), 129.8 (C-arom), 133.2 (C-arom), 146.7 (C-3), 165.4 [O*C*(O)Ph], 168.2 [*C*(O)OEt].
IR (film): ν = 2958, 2930, 2869, 2359, 1722, 1650, 1451, 1367, 1266, 1192, 1096, 1070, 1026, 750, 713 cm^{-1}.
MS (DI, CI, NH_3): *m/z* = 346 ($MH^+ + NH_3$), 329 (MH^+), 285, 279, 164, 102.

Stannylations of Alkynes 11a, 12a and 12b; General Procedure:
Method A, Palladium(0)-catalyzed hydrostannylation (*Pd Stannylation*): To a solution of alkyne derivative in THF (0.1 to 0.3 M) and $PdCl_2(PPh_3)_2$ (0.02 equiv) was added Bu_3SnH (1.2 equiv) over a period of ca 1–2 min. Towards the end of the addition, the originally light yellow solution abruptly turned orange-brown, and H_2 evolution was observed, signaling the formation of $(Bu_3Sn)_2$. After stirring at 20 °C for 10 min, the dark brown mixture was concentrated in vacuo. The crude product was purified by flash chromatography on basic silica gel (Et_2O/petroleum ether, 0:100 to 50:50).
Method B, Stannylcupration with $(Bu_3Sn)_2CuCNLi_2$ (*Homocuprate*): To a solution of $(Bu_3Sn)_2$ (8.0 equiv) in anhyd THF (0.1 to 0.3 M) was added BuLi (1.6 M solution in hexane, 8.0 equiv) at –78 °C. The solution was stirred 30 min at –40 °C. Then the mixture was added via cannula to a suspension of CuCN (4.0 equiv) in anhyd THF (1 M) at –78 °C. The mixture was stirred at –40 °C until a yellow solution was obtained and cooled to –78 °C. Then a solution of alkyne in anhyd THF was added via cannula. The mixture was allowed to warm to the appropriate temperature and when the starting material had been consumed, the mixture was quenched by addition of brine. The mixture was diluted with Et_2O and the organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. The crude product was purified by flash chromatography on basic silica gel (Et_2O/petroleum ether, 0:100 to 50:50).
Method C, Stannylcupration with $(Bu_3Sn)_2CuCNLi_2$ and internal quenching with MeOH (*Homocuprate*/*MeOH*): To a solution of $(Bu_3Sn)_2$ (8.0 equiv) in anhyd THF (0.1 to 0.3 M) was added BuLi (1.6 M solution in hexane, 8.0 equiv) at –78 °C. The solution was stirred 30 min at –40 °C. Then the mixture was added via cannula to a suspension of CuCN (4.0 equiv) in anhyd THF (1 M) at –78 °C. The mixture was stirred at –40 °C until a yellow solution was obtained and cooled to –78 °C. Then anhyd MeOH (110 equiv) was added and the yellow solution turned to a red gel. The temperature was allowed to warm to –40 °C for 15 min until the gel was converted to a red solution. The red solution was cooled to –78 °C before the addition via cannula of a solution of alkyne in THF. The mixture was allowed to warm to the appropriate temperature and when the starting material had been consumed, the mixture was quenched by addition of brine. The mixture was diluted with Et_2O and the organic layer was washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. The crude product was purified by flash chromatography on basic silica gel (Et_2O/petroleum ether, 0:100 to 50:50).

Stannylations of 11a; (1*E*,3*R/S*,6*S*)-6-Methyl-7-[(tetrahydropyran)-2-yloxy]-1-[(tributyl)stannyl]hept-1-en-3-ol (13a), (3*R/S*,6*S*)-6-Methyl-7-[(tetrahydropyran)-2-yloxy]-2-[(tributyl)stannyl]-hept-1-en-3-ol (14a) and (1*Z*,3*R/S*,6*S*)-1,2-{Bis[(tributyl)stannyl]}-6-methyl-7-[(tetrahydropyran)-2-yloxy]hept-1-en-3-ol (15a):
Entry 1, Table 1 : Method A, *Pd Stannylation*: From **11a** (100 mg, 0.44 mmol), stannane **13a** (132 mg, 58%) and stannane **14a** (33 mg, 14%) were obtained (72% , **13a/14a** = 80:20).
Entry 2, Table 1 : Method B, *Homocuprate*: From **11a** (80 mg, 0.35 mmol), stannane **13a** (30 mg, 16%), stannane **14a** (40 mg, 22%), vicinal bis(stannane) **15a** (134 mg, 48%) and starting material **11a** (11 mg, 14%) were obtained (86%, **13a**/**14a**/**15a** = 19:25:56).
Entry 3, Table 1 : Method C, *Homocuprate*/*MeOH*: From **11a** (80 mg, 0.35 mmol), stannane **13a** (68 mg, 38%), stannane **14a** (41 mg, 23%) and starting material **11a** (24 mg, 30%) were obtained (61%, **13a/14a** = 63:37).
Entry 4, Table 1 : Method C, *Homocuprate*/*MeOH*: From **11a** (80 mg, 0.35 mmol), stannane **13a** (108mg, 61%), stannane **14a** (36 mg, 20%) and starting material **11a** (8 mg, 10%) were obtained (81%, **13a/14a** = 75:25).

13a:
^{1}H NMR (400 MHz, $CDCl_3$), *four diastereomers*: δ = 0.92–0.85 [m, 18 H, CH_3-6 + 3 CH_2 + 3 CH_3, Sn(CH_2CH$_2$CH$_2$CH_3)$_3$], 1.34–1.27 [m, 7 H, OH + 3 CH_2, Sn(CH$_2$CH$_2$CH_2CH$_3$)$_3$], 1.42–1.92 [m, 17 H, H_2-4 + H_2-5+ H-6+ H_2-3'+ H_2-4'+ H_2-5' + 3 CH_2, Sn(CH$_2$CH_2CH$_2$CH$_3$)$_3$],

3.15 (dd, 0.5 H, *J* = 11.5, 9.1 Hz, Hb-7), 3.23 (t, 0.5 H, *J* = 9.4 Hz, Hb-7), 3.46–3.54 (m, 1.5 H, Hb-6' + 0.5Ha-7), 3.60 (t, 0.5 H, *J* = 9.5 Hz, Ha-7), 3.84 (td, 1 H, *J* = 7.9, 2.8 Hz, Ha-6'), 3.99–4.18 (m, 1 H, H-3), 4.56 (t, 1 H, *J* = 3.0 Hz, H-2'), 6.00 (dm, 1 H, *J* = 19.1 Hz, H-2), 6.12 (d, 1 H, *J* = 19.1 Hz, *J* ^{1}H - ^{117}Sn = *J* ^{1}H - ^{119}Sn = 71.2 Hz, H-1).

^{13}C NMR (100 MHz, $CDCl_3$), *four diastereomers*: δ = 9.4 [3 CH_2, Sn(*C*H_2CH$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = 326.8 Hz, *J* ^{13}C - ^{119}Sn = 341.2 Hz], 13.6 [3 CH_3, Sn(CH$_2$CH$_2$CH$_2$*C*H$_3$)$_3$], 17.2 (CH_3, CH_3-6), 19.5 (C-5'), 25.5 (C-4'), 27.2 [3 CH_2, Sn(CH$_2$CH$_2$*C*H$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 52.8 Hz], 29.1 [3 CH_2, Sn(CH$_2$*C*H$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 19.5 Hz], 29.3, 29.4 (C-5), 30.7 (C-3'), 33.3, 33.4 (C-6), 34.4 (C-4), 61.9 (C-6'), 72.4 (C-7), 75.5 (C-3, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 60.9 Hz), 75.7 (C-3, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 60.8 Hz), 98.7, 98.9 (C-2'), 127.3 (C-1, *J* ^{13}C - ^{117}Sn = *J*^{13}C - ^{119}Sn = 367.0 Hz), 151.3 (C-2).

IR (film): ν = 3444, 2925, 2870, 2852, 1601, 1463, 1376, 1200, 1120, 1062, 1032, 904, 868, 668 cm^{-1}.

MS (DI, CI, NH_3): *m/z* calculated from major ^{120}Sn isotope = 501 ($MH^+ - H_2O$), 461 ($M^+ - 57$, C_4H_9), 359, 308, 291, 244, 229, 162, 102, 85.

Anal. calc. for $C_{25}H_{50}O_3Sn$ (517.4): C, 58.04; H, 9.74; found C, 58.17; H, 9.88.

14a:

^{1}H NMR (400 MHz, $CDCl_3$), *four diastereomers*: δ = 0.87–0.97 [(m, 18 H, CH_3-6 + 3 CH_2 + 3 CH_3, Sn(C*H*$_2$CH$_2$CH$_2$C*H*$_3$)$_3$], 1.38–1.23 [m, 7 H, OH + 3 CH_2, Sn(CH$_2$CH$_2$C*H*$_2$CH$_3$)$_3$], 1.41–1.82 [m, 17 H, H_2-4 + H_2-5 + H-6 + H_2-3' + H_2-4' + H_2-5' + 3 CH_2, Sn(CH$_2$C*H*$_2$CH$_2$CH$_3$)$_3$], 3.18 (dd, 0.5 H, *J* = 9.4, 9.3 Hz, Hb-7), 3.25 (t, 0.5 H, *J* = 9.3 Hz, Hb-7), 3.48–3.57 (m, 1.5 H, 0.5 Ha-7 + Hb-6'), 3.62 (dd, 0.5 H, *J* = 9.4 , 9.2 Hz, Ha-7), 3.87 (td, 1 H, *J* = 8.3, 3.4 Hz, Ha-6'), 4.16–4.21 (m, 1 H, H-3), 4.57–4.59 (m, 1 H, H-2'), 5.22 (s, 1 H, *J* ^{1}H - ^{117}Sn = *J* ^{1}H - ^{119}Sn = 63.1 Hz, Ha-1), 5.79 (s, 1 H, *J* ^{1}H - ^{117}Sn = *J* ^{1}H - ^{119}Sn = 132.0 Hz, Hb-1).

^{13}C NMR (100 MHz, $CDCl_3$), *four diastereomers*: δ = 10.3 [3 CH_2, Sn(*C*H$_2$CH$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = 321.1 Hz, *J* ^{13}C - ^{119}Sn = 335.5 Hz], 13.8 [3 CH_3, Sn(CH$_2$CH$_2$CH$_2$*C*H$_3$)$_3$], 17.3, 17.4 (CH_3, CH_3-6), 19.7 (C-5'), 25.7 (C-4'), 27.5 [3 CH_2, Sn(CH$_2$CH$_2$*C*H$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 58.5 Hz], 29.2 [3 CH_2, Sn(CH$_2$*C*H$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 18.4 Hz], 29.8, 29.9 (C-5), 30.8 (C-3'), 33.5, 33.6 (C-6), 35.1 (C-4), 62.2, 62.3 (C-6'), 73.0, 73.1 (C-7), 79.9 (C-3, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 32.1 Hz), 99.0, 99.1 (C-2'), 123.9 (C-1, *J* ^{13}C - ^{117}Sn = *J*^{13}C - ^{119}Sn = 21.2 Hz), 124.1 (C-1, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 21.0 Hz), 159.4, 159.6 (C-2).

IR (film): ν = 3462, 2926, 2870, 2852, 1463, 1376, 1120, 1062, 1025, 978, 919, 904, 867, 806, 666 cm^{-1}.

MS (DI, CI, NH_3): *m/z* calculated from major ^{120}Sn isotope = 501 ($MH^+ - H_2O$), 359, 308, 291, 145, 102, 85.

Anal. calc. for $C_{25}H_{50}O_3Sn$ (517.4): C, 58.04; H, 9.74; found C, 58.24; H, 9.98.

15a:

^{1}H NMR (400 MHz, $CDCl_3$), *four diastereomers*: δ = 0.87–1.01 [m, 33 H, CH_3-6 + 6 CH_2 + 6 CH_3, 2 Sn(C*H*$_2$CH$_2$CH$_2$C*H*$_3$)$_3$], 1.28–1.39 [m, 13 H, OH + 6 CH_2, 2 Sn(CH$_2$CH$_2$C*H*$_2$CH$_3$)$_3$], 1.42–1.87 [m, 23 H, H_2-4 + H_2-5 + H-6 + H_2-3' + H_2-4' + H_2-5' + 6 CH_2, 2 Sn(CH$_2$C*H*$_2$CH$_2$CH$_3$)$_3$], 3.16 (dd, 0.5 H, *J* = 9.4, 9.3 Hz, Hb-7), 3.24 (dd, 0.5 H, *J* = 9.4z, 9.3 Hz, Hb-7), 3.47–3.55 (m, 1.5 H, Ha-7 + Hb-6'), 3.63 (dd, 0.5 H, *J* = 9.4, 9.3 Hz, Ha-7), 3.87 (td, 1 H, *J* = 8.3, 3.4 Hz, Ha-6'), 4.00–4.09 (m, 1 H, H-3), 4.57–4.59 (m, 1 H, H-2'), 6.75 (s, 1 H, *J* ^{1}H - ^{117}Sn^{a} = *J* ^{1}H - ^{119}Sn^{a} = 132.0 Hz, *J* ^{1}H - ^{117}Sn^{b} = *J* ^{1}H - ^{119}Sn^{b} = 66.5 Hz, H-1).

^{13}C NMR (50 MHz, $CDCl_3$), *four diastereomers*: δ = 11.1 [3 CH_2, Sn(*C*H$_2$CH$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = 318.4 Hz, *J* ^{13}C - ^{119}Sn = 333.5 Hz], 11.4 [3 CH_2, Sn(*C*H$_2$CH$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C -^{117}Sn = 309.3 Hz, *J* ^{13}C - ^{119}Sn = 324.1 Hz], 13.8 [6 CH_3, Sn(CH$_2$CH$_2$CH$_2$*C*H$_3$)$_3$], 17.4 (CH_3, CH_3-6), 19.7 (C-5'), 25.7 (C-4'), 27.5 [3 CH_2, Sn(CH$_2$CH$_2$*C*H$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C -^{119}Sn = 56.5 Hz], 27.7 [3 CH_2, Sn(CH$_2$CH$_2$*C*H$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 61.8 Hz], 29.3 [3 CH_2, Sn(CH$_2$*C*H$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 19.7 Hz], 29.5 [C-5, 3 CH_2, Sn(CH$_2$*C*H$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 17.7 Hz], 30.9 (C-3'), 33.5 (C-6), 34.9 (C-4), 62.3 (C-6'), 73.2 (C-7), 84.0 (C-3, *J* ^{13}C - ^{117}Sn^{b} = *J* ^{13}C - ^{119}Sn^{b} = 90.9 Hz, *J* ^{13}C - ^{117}Sn^{a} = *J* ^{13}C - ^{119}Sn^{a} = 46.2 Hz), 99.02, 99.2 (C-2'), 140.3 (C-1, *J* ^{13}C - ^{117}Sn^{a} = *J* ^{13}C - ^{119}Sn^{a} = 61.8 Hz), 172.2 (C-2, *J* ^{13}C - ^{117}Sn^{b} = *J* ^{13}C - ^{119}Sn^{b} = 30.3 Hz).

IR (film): ν = 3614, 3459, 2954, 2870, 2853, 1538, 1463, 1376, 1120, 1063, 1025, 865, 666 cm^{-1}.

MS (DI, CI, NH_3): *m/z* calculated from major ^{120}Sn isotope = 597, 595, 507, 443, 308, 291, 244, 160, 102, 85.

Anal. calc. for $C_{37}H_{76}O_3Sn_2$ (806.4): C, 55.11; H, 9.50; found C, 54.92; H, 9.59.

Stannylations of 12a; Ethyl (2*E*,4*S*,7*R/S*,8*E*)-2,4-Dimethyl-7-hydroxy-9-[(tributyl)stannyl]non-2,8-dienoate (16a), Ethyl (2*E*,4*S*,7*R/S*)-2,4-Dimethyl-7-hydroxy-8-[(tributyl)stannyl]non-2,8-dienoate (17a) and Ethyl (2*E*,4*S*,7*R/S*,8*Z*)-8,9-{Bis[(tributyl)stannyl]}-2,4-dimethyl-7-hydroxynon-2,8-dienoate (18a):

Entry 1, Table 2: Method A *Pd Stannylation*: From **12a** (65 mg, 0.29 mmol), stannane **16a** (54 mg, 37%) was obtained.

Entry 2, Table 2: Method B *Homocuprate*: From **12a** (50 mg, 0.22 mmol), stannane **17a** (9 mg, 8%), vicinal bis(stannane) **18a** (50 mg, 30%), and starting material **12a** (20 mg, 40%) were obtained (38%, **17a**/**18a** = 20:80).

Entry 3, Table 2: Method C *Homocuprate*/*MeOH*: From **12a** (50 mg, 0.22 mmol), stannane **16a** (40 mg, 35%), stannane **17a** (13 mg, 11%) and starting material **12a** (13 mg, 26%) were obtained (46%, **16a**/**17a** = 75:25).

16a:

^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.82–0.99 [m, 15 H, 3 CH_2 + 3 CH_3, Sn(C*H*$_2$CH$_2$CH$_2$C*H*$_3$)$_3$], 1.02 (d, 3 H, *J* = 6.8 Hz, CH_3-4), 1.29–1.35 [m, 9 H, C*H*$_3$CH$_2$O + 3 CH_2, Sn(CH$_2$CH$_2$C*H*$_2$CH$_3$)$_3$], 1.47–1.59 [m, 11 H, H_2-5 + H_2-6 + OH + 3 CH_2, Sn(CH$_2$C*H*$_2$CH$_2$CH$_3$)$_3$], 1.85 (d, 3 H, *J* = 1.4 Hz, CH_3-2), 2.48–2.57 (m, 1 H, H-4), 4.02–4.17 (m, 1 H, H-7), 4.20 (q, 2 H, *J* = 7.1 Hz, CH$_3$C*H*$_2$O), 5.98 (dd, 1 H, *J* = 19.1, 5.4 Hz, H-8), 6.18 (d, 1 H, *J* = 19.1 Hz, *J* ^{1}H - ^{117}Sn = *J* ^{1}H - ^{119}Sn = 69.7 Hz, H-9), 6.54 (dq, 1 H, *J* = 10.1, 1.4 Hz, H-3).

^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 9.56 [3 CH_2, Sn(*C*H$_2$CH$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = 342.3 Hz, *J* ^{13}C - ^{119}Sn = 327.1 Hz], 12.5 (*C*H$_3$CH$_2$O), 13.6 [3 CH_3, Sn(CH$_2$CH$_2$CH$_2$*C*H$_3$)$_3$], 14.3 (CH_3, CH_3-4), 19.9 (CH_3-2), 27.2 [3 CH_2, Sn(CH$_2$CH$_2$*C*H$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 53.1 Hz], 29.1 [3 CH_2, Sn(CH$_2$*C*H$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 19.4 Hz], 32.5, 32.6 (C-5), 33.2, 33.3 (C-4), 34.9 (C-6), 60.3 (CH$_3$*C*H$_2$O), 75.5 (C-7), 126.8 (C-2), 127.8 (C-9), 147.4 (C-3), 151.2 (C-8), 168.3 [*C*(O)OEt].

IR (film): ν = 3432, 2956, 2926, 2870, 2853, 1711, 1647, 1601, 1457, 1375, 1260, 1177, 1122, 1096, 1024, 990, 873, 794, 750, 689, 663 cm^{-1}.

MS (DI, CI, NH_3): *m/z* calculated from major ^{120}Sn isotope = 517 (MH^+), 499 ($MH^+ - H_2O$), 459, 443, 308, 291, 227, 209, 181, 135, 112, 72.

Anal. calc. for $C_{25}H_{48}O_3Sn$ (515.4): C, 58.27; H, 9.39; C, 58.68, H, 9.52.

17a:

^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.89–0.96 [m, 15 H, 3 CH_2 + 3 CH_3, Sn(C*H*$_2$CH$_2$CH$_2$C*H*$_3$)$_3$], 1.02 (d, 3 H, *J* = 6.6 Hz, CH_3-4), 1.29–1.35 [m, 10 H, C*H*$_3$CH$_2$O + OH + 3 CH_2, Sn(CH$_2$CH$_2$C*H*$_2$CH$_3$)$_3$], 1.43–1.53 [m, 11 H, H-4 + H_2-5 + H_2-6 + 3 CH_2, Sn(CH$_2$C*H*$_2$CH$_2$CH$_3$)$_3$], 1.85 (s, 3 H, CH_3-2), 2.46–2.55 (m, 1 H, H-4), 4.12–4.18 (m, 1 H, H-7), 4.19 (q, 2 H, *J* = 7.2 Hz, CH$_3$C*H*$_2$O), 5.22 (d, 1 H, *J* = 1.9 Hz, *J* ^{1}H - ^{117}Sn = *J* ^{1}H - ^{119}Sn = 62.5 Hz, Ha-9), 5.79 (d, 1 H, *J* = 1.9 Hz, *J* ^{1}H - ^{117}Sn = *J* ^{1}H - ^{119}Sn =

131.3 Hz, Hb-9), 6.53 (d, 1 H, J = 10.2 Hz, H-3).
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 10.7 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$], 12.7 (CH_3, CH_3CH_2O), 13.7 [3 CH_3, $Sn(CH_2CH_2CH_2CH_3)_3$], 14.4 (CH_3-4), 20.1 (CH_3-2), 27.5 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$, J ^{13}C - ^{117}Sn = J ^{13}C - ^{119}Sn = 51.5 Hz], 29.3 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$, J ^{13}C - ^{117}Sn = J ^{13}C - ^{119}Sn = 19.4 Hz], 33.1, 33.2 (C-5), 33.5 (C-4), 35.8 (C-6), 60.5 (CH_3CH_2O), 79.5 (C-7), 124.0 (C-9, J ^{13}C - ^{117}Sn = J ^{13}C - ^{119}Sn = 16.7 Hz), 127.1 (C-2), 147.5 (C-3), 159.8 (C-8), 168.4 [*C*(O)OEt].
IR (film): ν = 3497, 2956, 2927, 2870, 2853, 1711, 1696, 1648, 1375, 1257, 1180, 1119, 1080, 1024, 920, 874, 750 cm^{-1}.
MS (DI, CI, NH_3): *m/z* calculated from major ^{120}Sn isotope = 499 ($MH^+ - H_2O$), 457, 391, 364, 308, 291, 242, 209, 181, 135, 96.

18a:
^{1}H NMR (200 MHz, $CDCl_3$), *two diastereomers*: δ = 0.87–0.97 (m, 30 H, 6 CH_2 + 6 CH_3, 2 $Sn(CH_2CH_2CH_2CH_3)_3$], 1.01 (d, 3 H, J = 6.6 Hz, CH_3-4), 1.23–1.85 [m, 33 H, H-4 + H_2-5 + H_2-6 + OH + 6 CH_2, 2 $Sn(CH_2CH_2CH_2CH_3)_3$ + 6 CH_2, 2 $Sn(CH_2CH_2CH_2CH_3)_3$ + CH_3CH_2O], 1.85 (s, 3 H, CH_3-2), 2.42–2.58 (m, 1 H, H-4), 3.97–4.06 (m, 1 H, H-7), 4.18 (q, 2 H, J = 7.1 Hz, CH_3CH_2O), 6.53 (d, 1 H, J = 10.1 Hz, H-3), 6.74 (s, 1 H, J ^{1}H - ^{117}Sn^a = J ^{1}H - ^{119}Sn^a = 176.4 Hz, J ^{1}H - ^{117}Sn^b = J ^{1}H - ^{119}Sn^b = 66.2 Hz, H-9).
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 11.3 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$], 11.7 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$], 12.6 (CH_3CH_2O), 13.6 [6 CH_3, 2 $Sn(CH_2CH_2CH_2CH_3)_3$], 14.6 (CH_3-4), 20.1 (CH_3-2), 27.4 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$, J ^{13}C - ^{117}Sn = J ^{13}C - ^{119}Sn = 55.2 Hz], 27.6 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$, J ^{13}C - ^{117}Sn = J ^{13}C - ^{119}Sn = 60.8 Hz], 29.4 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$], 29.5 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$], 33.4 (C-5), 33.5 (C-4), 35.4 (C-6), 60.4 (CH_3CH_2O), 83.8, 84.0 (C-7), 127.0 (C-2), 140.6-140.9 (C-9), 147.5 (C-3), 168.4 (C-1), 172.1, 172.2 (C-8).
IR (film): ν = 3505, 2955, 2923, 2870, 2853, 2360, 1712, 1696, 1648, 1463, 1375, 1258, 1180, 1124, 1072, 1022, 960, 863, 750, 666 cm^{-1}.
MS (DI, CI, NH_3): *m/z* calculated from major ^{120}Sn isotope = 789 ($MH^+ - H_2O$), 787, 745, 597, 515, 457, 441, 308, 291, 209, 179, 135.
Anal. calc. for $C_{37}H_{74}O_3Sn_2$ (804.4): C, 55.25; H, 9.27; found C, 54.65; H, 9.29.

Stannylations of 12b; Ethyl (2*E*,4*S*,7*R/S*,8*E*)-2,4-Dimethyl-7-(benzoyloxy)-9-[(tributyl)stannyl]non-2,8-dienoate (16b) and Ethyl (2*E*,4*S*,7*R/S*)-2,4-Dimethyl-7-(benzoyloxy)-8-[(tributyl)-stannyl]non-2,8-dienoate (17b):
Method A, *Pd Stannylation*: From **12b** (1.05 g, 3.20 mmol), stannane **16b** (677 mg, 34%) and stannane **17b** (452 mg, 23%) were obtained (57%, **16b**/**17b** = 60:40).
Method C, *Homocuprate*/*MeOH*: From **12b** (50 mg, 0.15 mmol), stannane **16b** (35 mg, 37%) and starting material **12b** (11 mg, 22%) were obtained.

16b:
^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.83–0.95 [m, 15 H, 3 CH_2 + 3 CH_3, $Sn(CH_2CH_2CH_2CH_3)_3$], 1.02 (d, 3 H, J = 6.5 Hz, CH_3-4), 1.24–1.35 [m, 9 H, CH_3CH_2O + 3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$], 1.42–1.53 (m, 8 H, H_2-5 + 3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$], 1.68–1.87 (m, 2 H, H_2-6), 1.85 (s, 3 H, CH_3-2), 2.48–2.59 (m, 1 H, H-4), 4.19 (q, 2 H, J = 7.0 Hz, CH_3CH_2O), 5.42–5.49 (m, 1 H, H-7), 5.98 (dd, 1 H, J = 19.1, 5.8 Hz, H-8), 6.25 (d, 1 H, J = 19.1 Hz, J ^{1}H - ^{117}Sn = J ^{1}H - ^{119}Sn = 68.6 Hz, H-9), 6.53 (d, 1 H, J = 9.9 Hz, H-3), 7.46 (t, 2 H, J = 7.1 Hz, H-arom), 7.58 (t, 1 H, J = 7.2 Hz, H-arom), 8.07 (t, 2 H, J = 8.3 Hz, H-arom).
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 9.9 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$], 12.7 (CH_3CH_2O), 13.7 [3 CH_3, $Sn(CH_2CH_2CH_2CH_3)_3$], 14.4 (CH_3-4), 20.0 (CH_3-2), 27.3 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$, J ^{13}C - ^{117}Sn = J ^{13}C - ^{119}Sn = 51.0 Hz], 29.2 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$, J ^{13}C - ^{117}Sn = J ^{13}C - ^{119}Sn = 21.0 Hz], 32.4 (C-5 + C-6), 33.2, 33.3 (C-4), 60.5 (CH_3CH_2O), 77.4, 77.5 (C-7), 126.4 (C-2), 127.3 (C-9), 128.4 (C-arom), 129.8 (C-arom), 132.8 (C-arom), 146.0 (C-8), 147.1 (C-3), 165.9 [O*C*(O)Ph], 168.4 (C-1).
IR (film): ν = 2956, 2926, 2870, 1716, 1648, 1602, 1451, 1366, 1314, 1268, 1175, 1109, 1069, 1026, 988, 864, 749, 711 cm^{-1}.
MS (DI, CI, NH_3): *m/z* calculated from major ^{120}Sn isotope = 638 ($MH^+ + NH_3$), 621 (MH^+), 499, 497, 348, 308, 291, 226, 209, 122.

17b:
^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.83–0.95 [m, 15 H, 3 CH_2 + 3 CH_3, $Sn(CH_2CH_2CH_2CH_3)_3$], 1.02 (d, 3 H, J = 6.5 Hz, CH_3-4), 1.24–1.35 [m, 9 H, CH_3CH_2O + 3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$], 1.42–1.53 [m, 8 H, H_2-5 + 3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$], 1.68–1.87 (m, 2 H, H_2-6), 1.85 (s, 3 H, CH_3-2), 2.48–2.59 (m, 1 H, H-4), 4.19 (q, 2 H, J = 7.0 Hz, CH_3CH_2O), 5.24 (s, 1 H, J ^{1}H - ^{117}Sn = J ^{1}H - ^{119}Sn = 61.0 Hz, Ha-9), 5.56–5.62 (m, 1 H, H-7), 5.93 (s, 1 H, J ^{1}H - ^{117}Sn = J ^{1}H - ^{119}Sn = 125.0 Hz, Hb-9), 6.53 (d, 1 H, J = 9.9 Hz, H-3), 7.46 (t, 2 H, J = 7.1 Hz, H-arom), 7.58 (t, 1 H, J = 7.2 Hz, H-arom), 8.07 (t, 2 H, J = 8.3 Hz, H-arom).
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 9.9 [(3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$], 12.7 (CH_3CH_2O), 13.7 [3 CH_3, $Sn(CH_2CH_2CH_2CH_3)_3$], 14.4 (CH_3-4), 20.0 (CH_3-2), 27.3 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$, J ^{13}C - ^{117}Sn = J ^{13}C - ^{119}Sn = 51.0 Hz), 29.2 [3 CH_2, $Sn(CH_2CH_2CH_2CH_3)_3$, J ^{13}C - ^{117}Sn = J ^{13}C - ^{119}Sn = 21.0 Hz], 32.4 (C-5 + C-6), 33.2, 33.3 (C-4), 60.5 (CH_3CH_2O), 81.8 (C-7), 126.4 (C-9), 132.8, 132.7, 132.4, 131.4, 131.3, 129.8, 128.7, 128.4 (C-arom + C-8 + C-2), 147.1 (C-3), 165.9 [O*C*(O)Ph], 168.4 (C-1).
IR (film): ν = 2956, 2926, 2870, 1716, 1648, 1602, 1451, 1366, 1314, 1268, 1175, 1109, 1069, 1026, 988, 864, 749, 711 cm^{-1}.
MS (DI, CI, NH_3): *m/z* calculated from major ^{120}Sn isotope = 499 (MH^+ – 122, $PhCO_2H$), 497, 348, 308, 291, 226, 209, 122.

Ethyl (2*E*,4*S*)-7-(Benzoyloxy)-2,4-dimethylhept-2-enoate (19):
To a solution of **9** (4.55 g, 22.5 mmol) and DMAP (0.05 equiv) in anhyd CH_2Cl_2 (100 mL) at –30 °C were added Et_3N (18.8 mL, 135.0 mmol, 6.0 equiv) and benzoyl chloride (7.8 mL, 67.5 mmol, 3.0 equiv). The cold bath was removed and the mixture was stirred at 0 °C for 2 h. Then the mixture was diluted with Et_2O. The organic layer was washed with H_2O and brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 20:80) gave (2*S*)-5-(benzoyloxy)-2-methyl-1-[(tetrahydropyran)-2-yloxy]pentane (6.89 g, quantitative yield) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.98 (d, 1.5 H, J = 6.6 Hz, CH_3-2), 0.99 (d, 1.5 H, J = 6.6 Hz, CH_3-2), 1.27–1.33 (m, 1 H, Hb-3), 1.50–1.86 (m, 10 H, H-2 + Ha-3 + H_2-4 + H_2-3' + H_2-4' + H_2-5'), 3.22 (dd, 0.5 H, J = 9.5, 9.4 Hz, Hb-1), 3.26 (dd, 0.5 H, J = 9.5, 9.4 Hz, Hb-1), 3.48–3.53 (m, 1 H, Hb-6'), 3.61 (dd, 0.5 H, J = 9.6, 9.4 Hz, Ha-1), 3.63 (dd, 0.5 H, J = 9.6, 9.4 Hz, Ha-1), 3.83–3.89 (m, 1 H, Ha-6'), 4.33 (t, 2 H, J = 6.6 Hz, H_2-5), 4.59 (t, 1 H, J = 3.1 Hz, H-2'), 7.44 (t, 2 H, J = 8.0 Hz, H-arom), 7.50–7.58 (m, 1 H, H-arom), 8.06 (d, 2 H, J = 8.0 Hz, H-arom).
^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 17.1, 17.2 (CH_3-2), 19.6 (C-5'), 25.6 (C-4'), 26.3 (C-4), 30.1 (C-3), 30.8 (C-3'), 33.3 (C-2), 62.2 (C-6'), 65.4 (C-5), 72.8 (C-1), 99.1 (C-2'), 128.4 (C-arom), 129.6 (C-arom), 130.7 (C-arom), 132.9 (C-arom), 166.7 [O*C*(O)Ph].
IR (film): ν = 3063, 2949, 2871, 1790, 1719, 1601, 1584, 1452, 1382, 1314, 1275, 1212, 1174, 1116, 1072, 1033, 904, 867, 712 cm^{-1}.
MS (DI, CI, NH_3): *m/z* = 324 ($MH^+ + NH_3$), 307 (MH^+), 240, 223, 205, 184, 154, 118, 102, 85.

To a solution of (2*S*)-5-(benzoyloxy)-2-methyl-1-[(tetrahydropyran)-2-yloxy]pentane (7.0 g, 22.8 mmol) in MeOH (200 mL) at r.t. was added TsOH (1.30 g, 6.85 mmol, 0.3 equiv) and the mixture was stirred at r.t. for 1 h. Then it was quenched by the addition of Et_3N (1.9 mL, 13.7 mmol, 0.6 equiv). After 5 min, the MeOH was removed under reduced pressure and the residue was taken up in CH_2Cl_2. The res-

idue was washed with H_2O and the aqueous layer was separated and extracted with CH_2Cl_2 (2 × 200 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 50:50 to 80:20) gave (2*S*)-5-(benzoyloxy)-2-methylpentan-1-ol (4.10 g, 81%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (d, 3 H, *J* = 6.7 Hz, CH_3-2), 1.26–1.36 (m, 1 H, Hb-3), 1.58–1.65 (m, 1 H, Ha-3), 1.67–1.76 (m, 1 H, H-2), 1.76–1.82 (m, 1 H, Hb-4), 1.84–1.93 (m, 1 H, Ha-4), 3.47–3.55 (m, 3 H, H_2-1 + OH), 4.34 (t, 2 H, *J* = 6.7 Hz, H_2-5), 7.46 (t, 2 H, *J* = 7.6 Hz, H-arom), 7.57 (t, 1 H, *J* = 7.6 Hz, H-arom), 8.05 (d, 2 H, *J* = 7.6 Hz, H-arom).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.6 (CH_3-2), 26.6 (C-4), 29.9 (C-3), 35.8 (C-2), 65.4 (C-5), 68.3 (C-1), 128.5 (C-arom), 129.7 (C-arom), 131.0 (C-arom), 132.9 (C-arom), 166.8 [O*C*(O)Ph].

IR (film): ν = 3420, 2954, 1718, 1602, 1451, 1387, 1315, 1276, 1176, 1113, 1070, 1026, 711 cm^{-1}.

MS (DI, CI, NH_3): *m*/*z* = 240 ($MH^+ + NH_3$), 223 (MH^+), 240, 221, 139, 122, 101, 78, 61.

Anal. calc. for $C_{13}H_{18}O_3$ (222.3): C, 70.25; H, 8.16; found C, 70.01; H, 8.24.

To a solution of oxalyl chloride (6.4 mL, 73.6 mmol, 4.0 equiv) in anhyd CH_2Cl_2 (200 mL) at –55 °C was added DMSO (11.4 mL, 147.2 mmol, 8.0 equiv). This was followed 5 min later with the addition via cannula of a solution of alcohol (2*S*)-5-(benzoyloxy)-2-methyl-pentan-1-ol (4.09 g, 18.4 mmol) in anhyd CH_2Cl_2 (50 mL). The resulting slurry was stirred for 1 h and Et_3N (53.9 mL, 386.4 mmol, 21.0 equiv) was added at this point and after 5 min, the mixture was warmed to r.t. The mixture was diluted with CH_2Cl_2 (200 mL) and washed with an ice-cold 2 M HCl solution (193 mL) and H_2O (193 mL). The aqueous phases were extracted with CH_2Cl_2 (300 mL), the organic layers were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The crude aldehyde (2*S*)-5-(benzoyloxy)-2-methylpentanal thus obtained was used without further purification.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.16 (d, 3 H, *J* = 7.1 Hz, CH_3-2), 1.40–1.48 (m, 1 H, Hb-3), 1.51–1.61 (m, 1 H, Ha-3), 1.77–1.90 (m, 2 H, H_2-4), 2.40–2.47 (m, 1 H, H-2), 4.36 (t, 2 H, *J* = 6.7 Hz, H-5), 7.46 (t, 2 H, *J* = 7.6 Hz, H-arom), 7.58 (t, 1 H, *J* = 7.6 Hz, H-arom), 8.06 (d, 2 H, *J* = 7.5 Hz, H-arom), 8.95 (d, 1 H, *J* = 1.7 Hz, H-1).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.5 (CH_3-2), 26.3 (C-4), 27.0 (C-3), 46.0 (C-2), 64.7 (C-5), 128.5 (C-arom), 129.6 (C-arom), 130.3 (C-arom), 133.1 (C-arom), 166.7 [O*C*(O)Ph], 204.6 (C-1).

IR (film): ν = 2960, 1718, 1602, 1452, 1387, 1315, 1275, 1176, 1113, 1070, 1026, 713 cm^{-1}.

MS (GC, CI, NH_3): *m*/*z* = 238 ($MH^+ + NH_3$), 221 (MH^+), 105, 99.

A solution of preceding crude aldehyde (see above) and (ethoxycarbonylethylidene)triphenylphosphorane (14.1 g, 38.9 mmol, 2.1 equiv) in anhyd toluene (80 mL) was warmed at 50 °C for 9 h. Then toluene was removed under reduced pressure, the residue taken up in Et_2O, filtered on a pad of Celite and the solid was washed with Et_2O. The combined filtrate and washings were concentrated in vacuo. Purification of the residue by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 30:70) gave **19** (4.37 g, 78% for two steps) as a colorless oil.

19:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (d, 3 H, *J* = 6.6 Hz, CH_3-4), 1.32 (t, 3 H, *J* = 7.1 Hz, , C*H*$_3$CH$_2$O), 1.42–1.50 (m, 1 H, Hb-5), 1.53–1.62 (m, 1 H, Ha-5), 1.71–1.79 (m, 2 H, H_2-6), 1.86 (d, 3 H, *J* = 1.3 Hz, CH_3-2), 2.54–2.62 (m, 1 H, H-4), 4.21 (q, 2 H, *J* = 7.1 Hz, CH_3CH_2O), 4.32 (t, 2 H, *J* = 6.5 Hz, H_2-7), 6.56 (d, 1 H, *J* = 10.1 Hz, H-3), 7.46 (t, 2 H, *J* = 7.5 Hz, H-arom), 7.58 (t, 1 H, *J* = 7.5 Hz, H-arom), 8.05 (d, 2 H, *J* = 7.5 Hz, H-arom).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.7 (*C*H$_3$CH$_2$O), 14.4 (CH_3-4), 20.2 (CH_3-2), 26.9 (C-6), 33.1 (C-4), 33.2 (C-5), 60.6 (CH_3CH_2O), 65.0 (C-7), 127.1 (C-2), 128.5 (C-arom), 129.7 (C-arom), 130.5 (C-arom), 133.0 (C-arom), 147.2 (C-3), 166.8 [O*C*(O)Ph], 168.5 (C-1).

IR (film): ν = 2959, 1718, 1650, 1602, 1452, 1367, 1314, 1274, 1201, 1175, 1112, 1070, 1026, 712 cm^{-1}.

MS (GC, CI, NH_3): *m*/*z* = 322 ($MH^+ + NH_3$), 305 (MH^+), 276, 259, 231, 199, 182, 154, 136, 122, 105, 94.

Anal. calc. for $C_{18}H_{24}O_4$ (304.4): C, 71.03; H, 7.95; found C, 70.85; H, 7.84.

Ethyl (2*E*,4*S*)-2,4-Dimethyl-7-oxohept-2-enoate (20):

A solution of **19** (4.37 g, 14.3 mmol) and anhyd K_2CO_3 (2.97 mg, 21.5 mmol, 1.5 equiv) in anhyd MeOH (70 mL) was stirred for 8 h at 40 °C. Then the mixture was extracted with Et_2O and washed with H_2O and brine. The organic layer was dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 50:50 to 60:40) gave ethyl (2*E*,4*S*)-2,4-dimethyl-7-hydroxyhept-2-enoate (2.49 g, 87%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (d, 3 H, *J* = 6.5 Hz, CH_3-4), 1.31 (t, 3 H, *J* = 6.9 Hz, CH_3CH_2O), 1.37–1.42 (m , 2 H, Hb-5 + OH), 1.47–1.58 (m, 3 H, H_2-6 + Ha-5), 1.85 (d, 3 H, *J* = 1.4 Hz, CH_3-2), 2.51–2.55 (m, 1 H, H-4), 3.63 (t, 2 H, *J* = 6.2 Hz, H_2-7), 4.20 (q, 2 H, *J* = 6.9 Hz, CH_3CH_2O), 6.55 (dq, 1 H, *J* = 10.2, 1.4 Hz, H-3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.6 (*C*H$_3$CH$_2$O), 14.4 (CH_3-4), 20.0 (CH_3-2), 30.9 (C-6), 33.3 (C-5), 33.4 (C-4), 60.5 (CH_3CH_2O), 63.1 (C-7), 127.1 (C-2), 147.4 (C-3), 168.5 (C-1).

IR (film): ν = 3405, 2931, 2870, 1708, 1647, 1456, 1367, 1254, 1188, 1130, 1094, 1056, 1030, 750 cm^{-1}.

MS (GC, CI, NH_3): *m*/*z* = 218 ($MH^+ + NH_3$), 201 (MH^+), 172, 155, 137, 109, 95, 85, 58.

Anal. calc. for $C_{11}H_{20}O_3$ (200.3): C, 65.97; H, 10.07; found C, 65.81; H, 9.95

To a solution of oxalyl chloride (785 µL, 8.99 mmol, 1.2 equiv) in anhyd CH_2Cl_2 (25 mL) at –55 °C was added DMSO (1.4 mL, 18.0 mmol, 2.4 equiv). This was followed 5 min later with the addition via cannula of a solution of ethyl (2*E*,4S)-2,4-dimethyl-7-hydroxyhept-2-enoate (1.50 g, 7.49 mmol) in anhyd CH_2Cl_2 (10 mL). The resulting slurry was stirred for 1 h and Et_3N (5.2 mL, 37.5 mmol, 5.0 equiv) was then added and 5 min later the mixture was warmed to r.t. The solution was diluted with CH_2Cl_2 (80 mL) and was washed with an ice-cold 1 M HCl solution (38 mL) and H_2O (38 mL). The aqueous phases were extracted with CH_2Cl_2 (80 mL). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 10:90 to 40:60) gave **20** (1.18 g, 80%) as a colorless oil.

20:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (d, 3 H, *J* = 6.6 Hz, CH_3-4), 1.31 (t, 3 H, *J* = 7.1 Hz, C*H*$_3$CH$_2$O), 1.59–1.66 (m, 1 H, Hb-5), 1.75–1.83 (m, 1 H, Ha-5), 1.84 (d, 3 H, *J* = 1.2 Hz, CH_3-2), 2.42 (t, 2 H, *J* = 8.0 Hz, H_2-6), 2.52–2.58 (m, 1 H, H-4), 4.20 (q, 2 H, *J* = 7.1 Hz, CH_3CH_2O), 6.49 (dq, 1 H, *J* = 10.2, 1.2 Hz, H-3), 9.25 (s, 1 H, H-7).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.4 (*C*H$_3$CH$_2$O), 14.2 (CH_3-4), 19.7 (CH_3-2), 28.9 (C-5), 32.6 (C-4), 41.7 (C-6), 60.3 (CH_3CH_2O), 127.8 (C-2), 145.8 (C-3), 167.9 (C-1), 201.1 (C-7).

IR (film): ν = 2961, 2930, 2871, 2720, 1709, 1649, 1458, 1389, 1367, 1257, 1194, 1132, 1094, 1031, 751 cm^{-1}.

MS (GC, CI, NH_3): *m*/*z* = 216 ($MH^+ + NH_3$), 199 (MH^+), 187, 170, 153, 142, 125, 109, 95, 81, 69.

Anal. calc.for $C_{11}H_{18}O_3$ (198.3): C, 66.64; H, 9.15; found C, 66.51; H 9.07.

Addition of (*E*)-1-Lithio-2-[(tributyl)stannyl]ethene to Aldehyde 10; (1*E*,3*R*/*S*,6*S*)-6-Methyl-7-[(tetrahydropyran)-2-yloxy]-1-[(tributyl)stannyl]hept-1-en-3-ol (13a):

To a solution of (*E*)-1,2-{bis[(tributyl)stannyl]ethene (9.12 g, 15.0 mmol, 2.0 equiv) in anhyd THF (80 mL) at –78 °C was added BuLi (1.6 M solution in hexane, 8.0 mL, 12.8 mmol, 1.7 equiv). The mixture was stirred for 2 h at –40 to –15 °C. Then the mixture was

cooled at –78 °C and a solution of freshly prepared aldehyde **10** (1.51 g, 7.52 mmol) in anhyd THF (10 mL) was added via cannula. After stirring for 20 min, the mixture was quenched by the addition of satd aq NH_4Cl solution. The mixture was allowed to warm to r.t. and then extracted with Et_2O (300 mL). The combined extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 50:50) gave **13a** (3.70 g, 95%) as a colorless oil.

Addition of (*E*)-1-Lithio-2-[(tributyl)stannyl]ethene to Aldehyde 20; Ethyl (2*E*,4*S*,7*R*/*S*,8*E*)-2,4-Dimethyl-7-hydroxy-9-[(tributyl)stannyl]non-2,8-dienoate (16a), [2*R*/*S*(9*E*),3*E*,5*S*,8*R*/*S*(11*E*)]-2,8-{Bis[(tributyl)stannylethenyl]}-3,5-dimethyl-2-hydroxy-oxacyclooct-3-ene (21) and Ethyl (1*E*,4*E*,6*S*,9*R*/*S*,10*E*)-1,11-{Bis[(tributyl)stannyl]}-4,6-dimethyl-9-hydroxy-3-oxaundeca-1,4,10-trienoate (22):

To a solution of (*E*)-1,2-{bis[(tributyl)stannyl]ethene (3.46 g, 5.71 mmol, 2.0 equiv) in anhyd THF (30 mL) at –78 °C was added BuLi (1.6 M solution in hexane, 3.03 mL, 4.85 mmol, 1.7 equiv). The mixture was stirred for 2 h at –40 to –25 °C, then cooled to –78 °C and a solution of freshly prepared aldehyde **20** (566 mg, 2.85 mmol) in anhyd THF (5 mL) was added via cannula. After stirring for 15 min, the mixture was quenched by the addition of satd aq NH_4Cl solution. The mixture was allowed to warm to r.t. and then extracted with Et_2O (200 mL). The combined extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 50:50) gave **16a** (590 mg, 40%), **21** (202 mg, 9%) and **22** (157 mg, 7%) as colorless oils.

To a solution of (*E*)-1,2-{bis[(tributyl)stannyl]ethene (1.63 g, 2.69 mmol, 1.3 equiv) in anhyd THF (30 mL) at –78 °C was added BuLi (1.6 M solution in hexane, 1.3 mL, 2.07 mmol, 1.0 equiv). The mixture was stirred for 2 h at –40 to –25 °C, then cooled to –78 °C and a solution of freshly prepared aldehyde **20** (410 mg, 2.07 mmol) in anhyd THF (5 mL) was added via cannula. After stirring for 10 min, the mixture was quenched by the addition of satd aq NH_4Cl solution. The mixture was allowed to warm to r.t. and then extracted with Et_2O (200 mL). The combined extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 50:50) gave **16a** (661 mg, 62%) as a colorless oil.

21:

^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.85–0.96 [m, 30 H, 6 CH_2 + 6 CH_3, 2 Sn(C*H*$_2$CH$_2$CH$_2$C*H*$_3$)$_3$], 0.99 (d, 3 H, *J* = 6.7 Hz, CH_3-4), 1.27–1.36 [m, 12 H, 6 CH_2, 2 Sn(CH$_2$CH$_2$C*H*$_2$CH$_3$)$_3$], 1.47–1.55 [m, 17 H, H_2-6 + H_2-7 + OH + 6 CH_2, 2 Sn(CH$_2$C*H*$_2$CH$_2$CH$_3$)$_3$], 1.61 (d, 3 H, *J* = 1.3 Hz, CH_3-3), 2.33–2.44 (m, 1 H, H-5), 4.00–4.06 (m, 1 H, H-8), 5.32 (d, 1 H, *J* = 9.3 Hz, H-4), 5.99 (dd, 0.5 H, *J* = 19.1, 5.5 Hz, H-11), 6.00 (dd, 0.5 H, *J* = 19.1, 5.5 Hz, H-11), 6.07 (d, 1 H, *J* = 19.3 Hz, H-9 or H-10), 6.13 (d, 1 H, *J* = 19.1 Hz, H-12), 6.20 (d, 1 H, *J* = 19.3 Hz, *J* ^{1}H - ^{117}Sn = *J* ^{1}H - ^{119}Sn = 72.8 Hz, H-9 or H-10).

^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 9.95 [6 CH_2, 2 Sn(*C*H$_2$CH$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = 326.1 Hz, *J* ^{13}C - ^{119}Sn = 340.2 Hz], 13.0 (CH_3-5), 13.7 [6 CH_3, 2 Sn(CH$_2$CH$_2$CH$_2$*C*H$_3$)$_3$], 20.9 (CH_3-3), 27.3 [6 CH_2, Sn(CH$_2$CH$_2$*C*H$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 51.9 Hz], 29.3 [6 CH_2, 2 Sn(CH$_2$CH$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 19.9 Hz], 32.7, 32.8 (C-5), 33.3, 33.5 (C-6), 35.1, 35.3 (C-7), 75.7, 75.9 (C-8), 82.3 (C-2, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 56.1 Hz), 126.1 (C-10), 127.8 (C-12), 133.2 (C-4), 136.8 (C-3), 151.6, 151.7 (C-9 + C-11).

IR (film): ν = 3440, 2955, 2924, 2870, 2852, 1668, 1588, 1463, 1376, 1182, 1071, 992, 874, 666 cm^{-1}.

MS (DI, CI, NH_3): *m/z* calculated from major ^{120}Sn isotope = 757 (MH^+ – 32), 597, 595, 525, 478, 401, 308, 291, 235, 207, 72.

22:

^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 0.86–0.93 [m, 30 H, 6 CH_2 + 6 CH_3, 2 Sn(C*H*$_2$CH$_2$CH$_2$C*H*$_3$)$_3$], 1.04 (d, 3 H, *J* = 6.8 Hz, CH_3, CH_3-6), 1.28–1.34 [m, 12 H, 6 CH_2, 2 Sn(CH$_2$CH$_2$C*H*$_2$CH$_3$)$_3$], 1.47–1.53 [m, 16 H, H_2-7 + H_2-8 + 6 CH_2, 2 Sn(CH$_2$C*H*$_2$CH$_2$CH$_3$)$_3$], 1.80 (s, 3 H, CH_3-4), 2.53–2.64 (m, 1 H, H-6), 3.35–3.40 (m, 1 H, OH), 3.99–4.18 (m, 1 H, H-9), 5.98 (dd, 0.5 H, *J* = 19.1, 5.5 Hz, H-10), 5.99 (dd, 0.5 H, *J* = 19.1, 5.5 Hz, H-10), 6.07 (d, 1 H, *J* = 19.3 Hz, H-1 or H-2), 6.15 (d, 1 H, *J* = 19.1 Hz, H-11), 6.29 (d, 1 H, *J* = 19.3 Hz, *J* ^{1}H - ^{117}Sn = *J* ^{1}H - ^{119}Sn = 71.9 Hz, H-1 or H-2), 6.40 (d, 1 H, *J* = 9.6 Hz, H-5).

^{13}C NMR (50 MHz, $CDCl_3$): *two diastereomers:* δ = 9.9 [6 CH_2, 2 Sn(*C*H$_2$CH$_2$CH$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = 326.1 Hz, *J* ^{13}C - ^{119}Sn = 322.8 Hz], 11.2, 11.9 (CH_3-6), 13.7 [6 CH_3, 2 Sn(CH$_2$CH$_2$CH$_2$*C*H$_3$)$_3$], 20.1 (CH_3-4), 27.3 [6 CH_2, Sn(CH$_2$CH$_2$*C*H$_2$CH$_3$)$_3$, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 52.0 Hz], 29.3 [6 CH_2, 2 Sn(CH$_2$CH$_2$CH$_2$CH$_3$)$_3$], 32.8 (C-7), 33.8 (C-6), 35.1, 36.8 (C-8), 75.6 (C-9, *J* ^{13}C - ^{117}Sn = *J* ^{13}C - ^{119}Sn = 48.0 Hz), 128.3 (C-11), 131.4 (C-2), 135.9 (C-4), 147.9 (C-5), 151.2 (C-10), 151.5 (C-1), 200.3 (C-3).

IR (film): ν = 3424, 2956, 2925, 2870, 2852, 1668, 1635, 1376, 1070, 990, 874 cm^{-1}.

MS (DI, CI, NH_3): *m/z* calculated from major ^{120}Sn isotope = 597, 595, 525, 467, 345, 308, 291, 235, 207, 199, 125, 72.

Coupling Reactions Between the Iodo Derivative 3 and Stannane 13a; General Procedures:

Method 1, *($Ph_3P)_4Pd$ in THF or DMF*: To a flame-dried flask under a purge of argon was added the vinyl iodide **3** (1 equiv).[18] The appropriate solvent was added and the mixture was degassed 3 times by evacuating to 0.06 Torr and flushing with argon. $(Ph_3P)_4Pd$ (0.1 equiv) was then added and 5 min later a deoxygenated (vide infra) solution of the vinyl stannane **13a** (1 equiv) was added via cannula. The mixture was then stirred at r.t. overnight, then taken up in Et_2O (30 mL). The organic layer was washed with H_2O (3 × 10 mL) and concentrated in vacuo. The residue was dissolved in Et_2O (5 mL) and treated with aq 1 M KF solution (4 equiv). After stirring for 2 h at r.t., the mixture was filtered on a pad of Celite. The organic layer was decanted, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification was performed by flash chromatography on silica gel (Et_2O/petroleum ether, 40:60 to 100:0).

Method 2, *PdL_4 prepared from tris(dibenzylideneacetone)dipalladium(0), PPh_3, or PFu_3, or $AsPh_3$ as ligands, and CuI in DMF or NMP*: To a flame-dried flask under a purge of argon were added tris(dibenzylideneacetone)dipalladium(0) (0.05 equiv) and the appropriate ligand (0.2 equiv). The corresponding solvent was added and the mixture was degassed 3 times by evacuating to 0.06 Torr and flushing with argon. A solution of deoxygenated (vide infra) vinyl iodide **3** (1 equiv) was added via cannula and 5 min later a solution of deoxygenated (vide infra) vinyl stannane **13a** (1 equiv) was added via cannula. Then, solid CuI (0.1 equiv) was added to the mixture, which was stirred at r.t. for overnight. The mixture was dissolved in Et_2O (30 mL) and washed with H_2O (3 × 10 mL). The organic layer was concentrated in vacuo and the residue was dissolved in Et_2O (5 mL) and treated with aq 1M KF solution (4 equiv). After stirring for 2 h at r.t., the mixture was filtered on a pad of Celite. The organic layer was decanted, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification was performed by flash chromatography on silica gel (Et_2O/petroleum ether, 40:60 to 100:0).

Method 3, *$PdCl_2(MeCN)_2$, DMF, 20°C*: To a flame-dried flask under a purge of argon were added the vinyl stannane **13a** (1 equiv) and vinyl iodide **3** (1.3 equiv). DMF was added and the mixture was degassed 3 times by evacuating to 0.06 Torr and flushing with argon. Then $PdCl_2(MeCN)_2$ (0.04 equiv) was added and the mixture stirred at r.t. After 12 h and 24 h additional portions of the palladium catalyst (0.02 equiv) were added. After 36 h, the mixture was dissolved in Et_2O (30 mL) and washed with H_2O (3 × 10 mL). The organic layer was concentrated in vacuo and the residue was taken up in Et_2O

(5 mL) and treated with aq 1 M KF solution (4 equiv). After stirring for 2 h at r.t., the mixture was filtered on a pad of Celite. The organic layer was decanted, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification was performed by flash chromatography on silica gel (Et_2O/petroleum ether, 40:60 to 100:0).

(2E,4E,6E,8R/S,11S)-12-[(Tetrahydropyran)-2-yloxy]-3,5,11-trimethyldodeca-2,4,6-triene-1,8-diol **(23)**:
Entry 12, Table 3, Method 3, [$PdCl_2(MeCN)_2$, DMF, 20 °C]: from vinyl iodide **3** (6.6 g, 27.7 mmol) and stannane **13a** (10.7 g, 20.7 mmol), triene **23** (5.2 g, 75%) was obtained after 36 h at 20 °C.
^{1}H NMR (400 MHz, $CDCl_3$), *four diastereomers*: δ = 0.94 (d, 1.5 H, *J* = 6.7 Hz, CH_3-11), 0.95 (d, 1.5 H, *J* = 6.7 Hz, CH_3-11), 1.26–1.79 (m, 13 H, 2 OH + H_2-9 + H_2-10 + H-11 + H_2-3' + H_2-4' + H_2-5'), 1.81 (s, 3 H, CH_3-3), 1.91 (s, 3 H, CH_3-5), 3.17 (t, 0.5 H, *J* = 9.4 Hz, Hb-12), 3.22 (dd, 0.5 H, *J* = 9.4, 9.3 Hz, Hb-12), 3.47–3.54 (m, 1.5 H, 0.5Ha-12 + Hb-6'), 3.60 (dd, 0.5 H, *J* = 9.5, 9.4 Hz, Ha-12), 3.83–3.87 (m, 1 H, Ha-6'), 4.12–4.18 (m, 1 H, H-8), 4.26 (d, 2 H, *J* = 6.6 Hz, H_2-1), 4.52–4.60 (m, 1 H, H-2'), 5.57 (t, 1 H, *J* = 6.7 Hz, H-2), 5.66 (dd, 1 H, *J* = 15.6, 6.6 Hz, H-7), 5.68 (dd, 1 H, *J* = 15.6, 6.6 Hz, H-7), 5.89 (s, 1 H, H-4), 6.24 (d, 1 H, *J* = 15.6 Hz, H-6).
^{13}C NMR (50 MHz, $CDCl_3$), *four diastereomers*: δ = 14.0 (CH_3-5), 17.0 (CH_3-3), 17.1 (CH_3-11), 19.6 (C-5'), 25.6 (C-4'), 29.7 (C-10), 30.8 (C-3'), 33.6 (C-11), 35.2 (C-9), 59,7 (C-1), 62.4 (C-6'), 73.0, 73.1 (C-12), 73.5 (C-8), 99.1, 99.2 (C-2'), 129.7 (C-2), 131.9 (C-7), 133.9 (C-5), 134.6 (C-4), 135.0 (C-3), 135.8, 136.2(C-6).
IR (film): ν = 3425, 2934, 2871, 1669, 1455, 1378, 1200, 1121, 1061, 1031, 976, 904, 868, 815 cm^{-1}.
MS (DI, CI, NH_3): *m/z* = 356 ($MH^+ + NH_3$), 321 ($MH^+ - H_2O$), 303, 291, 237, 219, 201, 169, 118, 102, 85, 58.
Anal. calc. for $C_{20}H_{34}O_4$ (338.5): C, 70.97, H, 10.12; found C, 71.10; H, 10.35.

(2E,4E,7R/S,10S)-6-Methylene-11-[(tetrahydropyran)-2-yloxy]-3,5,10-trimethylundeca-2,4-diene-1,7-diol (**24**):
Entry 10, Table 3, Method 2, via PdL_4 prepared from tris(dibenzylideneacetone)dipalladium(0), $AsPh_3$ as ligand in DMF at 20 °C and CuI (10% mol): from vinyl iodide **3** (330 mg, 1.4 mmol) and stannane **13a** (535 mg, 1.04 mmol), a mixture of trienes **23** and **24** (260 mg, 74%, **23**/**24** = 60:40) was obtained after 12 h at 20 °C.

24 :
^{1}H NMR (400 MHz, $CDCl_3$), *four diastereomers*: δ = 0.93 (d, 1.5 H, *J* = 6.7 Hz, CH_3-10), 0.96 (d, 1.5 H, *J* = 6.7 Hz, CH_3-10), 1.83–1.18 (m, 13 H, 2 OH + H_2-8 + H_2-9 + H-10 + H_2-3' + H_2-4' + H_2-5'), 1.81 (s, 3 H, CH_3-3), 1.96 (s, 3 H, CH_3-5), 3.17 (dd, 0.5 H, *J* = 9.5, 9.4 Hz, Hb-11), 3.25 (dd, 0.5 H, *J* = 9.4, 9.3 Hz, Hb-11), 3.49–3.57 (m, 1.5 H, Hb-6', 0.5 Ha-11), 3.62 (dd, 0.5 H, *J* = 9.6, 9.5 Hz, Ha-11), 3.84 –3.89 (m, 1 H, Ha-6'), 4.27 (t, 2 H, *J* = 6.9 Hz, H_2-1), 4.43–4.51 (m, 1 H, H-7), 4.53–4.59 (m, 1 H, H-2'), 5.18 (s, 1 H, Hb-12), 5.25 (d, 1 H, *J* = 3.2 Hz, Ha-12), 5.55 (t, 1 H, *J* = 6.9 Hz, H-2), 6.00 (s, 1 H, H-4).
^{13}C NMR (50 MHz, $CDCl_3$), *four diastereomers*: δ = 13.7 (CH_3-5), 17.2, 17.5 (CH_3-10), 17.6 (CH_3-3), 18.4 (C-5'), 26.9 (C-4'), 30.2 (C-9), 30.9 (C-3'), 33.6 (C-10), 34.3, 34.4 (C-8), 59.7 (C-1), 62.4 (C-6'), 72.6, 72.8 (C-7), 73.1, 73.2 (C-11), 99.2, 99.3 (C-2'), 110.8 (C-12), 128.9 (C-2), 130.4 (C-4), 134.8 (C-5), 135.8 (C-3), 153.8, 154.0 (C-6).
IR (film): ν = 3395, 2942, 2870, 1652, 1599, 1454, 1378, 1353, 1261, 1200, 1137, 1120, 1076, 1062, 1024, 903, 867, 809 cm^{-1}.
MS (DI, CI, NH_3): *m/z* = 356 ($MH^+ + NH_3$), 338 ($MH^+ + NH_3 - H_2O$), 321 ($MH^+ - H_2O$), 303, 293, 254, 237, 219, 205, 183, 149, 132, 102, 85.
MS (DI, CI, NH_3, negative ion): *m/z* = 337 (MH^+), 336, 319, 291, 277, 269, 235, 221, 199, 179, 161, 148, 127, 119, 89.
Anal. calc. for $C_{20}H_{34}O_4$ (338.5): C, 70.97; H, 10.12; found C, 71.22; H, 10.48.

(2*E*,4*E*,6*E*,8*R/S*,11*S*)-1,8-[Bis(benzoyloxy)]-12-[(tetrahydropyran)-2-yloxy]-3,5,11-trimethyldodeca-2,4,6-triene (25):
To a solution of **23** (5.0 g, 14.9 mmol) and DMAP (0.02 equiv) in anhyd CH_2Cl_2 (80 mL) at –30 °C was added Et_3N (24.9 mL, 178.3 mmol, 12.0 equiv) and benzoyl chloride (10.3 mL, 89.2 mmol, 6.0 equiv). The cold bath was removed and the mixture was stirred at 0 °C for 2 h and at r.t. for 6 h. Then the mixture was diluted with Et_2O, the organic layer washed with H_2O and brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 0:100 to 40:60) gave **25** (6.74 g, 83%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$), *four diastereomers*: δ = 0.96 (d, 1.5 H, *J* = 6.5 Hz, CH_3-11), 0.97 (d, 1.5 H, *J* = 6.5 Hz, CH_3-11), 1.21–1.38 (m, 1 H, Hb-10), 1.44–1.62 (m, 5 H, Ha-10 + H_2-4' + H_2-5'), 1.63–1.75 (m, 1 H, H-11), 1.76–1.91 (m, 4 H, H_2-9 + H_2-3'), 1.91 (s, 3 H, CH_3-3 or CH_3-5), 1.93 (s, 3 H, CH_3-3 or CH_3-5), 3.20 (dd, 0.5 H, *J* = 9.5, 6.2 Hz, Hb-12), 3.24 (dd, 0.5 H, *J* = 9.5, 6.2 Hz, Hb-12), 3.48–3.54 (m, 1 H, Hb-6'), 3.56 (dd, 0.5 H, *J* = 9.0, 6.2 Hz, Ha-12), 3.60 (dd, 0.5 H, *J* = 9.5, 6.6 Hz, Ha-12), 3.68–3.88 (m, 1 H, Ha-6'), 4.53–4.59 (m, 1 H, H-2'), 4.95 (d, 2 H, *J* = 7.0 Hz, H_2-1), 5.57 (dt, 1 H, *J* = 7.2, 6.6 Hz, H-8), 5.63 (t, 1 H, *J* = 7.0 Hz, H-2), 5.73 (dd, 1 H, *J* = 15.6, 7.2 Hz, H-7), 5.97 (s, 1 H, H-4), 6.39 (d, 1 H, *J* = 15.6 Hz, H-6), 7.45 (t, 2 H, *J* = 7.6 Hz, H-arom), 7.46 (t, 2 H, *J* = 7.3 Hz, H-arom), 7.55 (t, 1 H, *J* = 7.2 Hz, H-arom), 7.57 (t, 1 H, *J* = 7.4 Hz, H-arom), 8.05 (d, 2 H, *J* = 6.8 Hz, H-arom), 8.08 (d, 2 H, *J* = 6.8 Hz, H-arom).
^{13}C NMR (50 MHz, $CDCl_3$), *four diastereomers*: δ = 13.9 (CH_3-5), 17.0 (CH_3-11), 17.3 (CH_3-3), 19.5 (C-5'), 25.6 (C-4'), 29.3, 29.4 (C-10), 30.8 (C-3'), 32.4 (C-9), 33.4 (C-11), 61.7 (C-1), 62.0 (C-6'), 72.7 (C-12), 75.6, 75.7 (C-8), 98.9 (C-2'), 124.4 (C-2), 127.1 (C-7), 128.2 (C-arom), 129.5 (C-arom), 132.7 (C-arom), 134.1 (C-3 or C-5), 135.1 (C-4), 137.8, 138.0 (C-6), 165.8, 166.4 [O*C*(O)Ph].
IR (film): ν = 2937, 1789, 1722, 1599, 1451, 1272, 1213, 1037, 1017, 996, 703 cm^{-1}.
MS (DI, CI, NH_3): *m/z* = 564 ($MH^+ + NH_3$), 527, 480, 442, 425, 358, 341, 303, 256, 219, 191, 139, 102, 78.
Anal. calc. for $C_{34}H_{42}O_6$ (546.7): C, 74.70; H, 7.74; found C, 74.58; H, 7.58.

(2*S*,5*R/S*,6*E*,8*E*,10*E*)-5,12-[Bis(benzoyloxy)]-2,8,10-trimethyldodeca-6,8,10-trien-1-ol (26) and [2*R*(1*E*,3*E*,5*E*),5*S*]-2-[7-(Benzoyloxy)-3,5-dimethylhepta-1,3,5-trien-1-yl]-5-methyloxaclyclohexane (27):
To a solution of **25** (417 mg, 0.76 mmol) in MeOH (15 mL) at r.t. was added TsOH (834 mg, 0.23 mmol, 0.3 equiv). The mixture was stirred at r.t. for 2.5 h and then quenched by the addition of Et_3N (64 µL, 0.46 mmol, 0.6 equiv). After 5 min the MeOH was removed under reduced pressure and the residue was dissolved in CH_2Cl_2. The organic layer was washed with H_2O and the aqueous layer separated and extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 50:50 to 60:40) gave **26** (269 mg, 80%) as a colorless oil.

To a solution of **25** (7.99 g, 14.6 mmol) in MeOH (200 mL) at r.t. was added TsOH (834 mg, 4.38 mmol, 0.3 equiv). The mixture was stirred at r.t. for 5 h and then quenched by the addition of Et_3N (650 µL, 4.68 mmol, 0.32 equiv). After 5 min the MeOH was removed under reduced pressure and the residue was taken up in CH_2Cl_2. The organic layer was washed with H_2O and the aqueous layer was separated and extracted with CH_2Cl_2 (2 × 300 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 50:50 to 60:40) gave **26** (1.68g, 34%) and **27** (2.76 g, 56%) as colorless oils.

26:
^{1}H NMR (400 MHz, $CDCl_3$), *four diastereomers*: δ = 0.96 (d, 3 H, *J* = 6.8 Hz, CH_3-2), 1.21–1.33 (m, 2 H, Hb-3 + OH), 1.52–1.62 (m, 1

H, Ha-3), 1.65–1.73 (m, 1 H, H-2), 1.82–1.88 (m, 1 H, Hb-4), 1.89–1.96 (m, 1 H, Ha-4), 1.91 (s, 3 H, CH_3-8 or CH_3-10), 1.93 (s, 3 H, CH_3-8 or CH_3-10), 3.44–3.56 (m, 2 H, H_2-1), 4.95 (d, 2 H, *J* = 7.0 Hz, H_2-12), 5.61–5.65 (m, 1 H, H-5), 5.64 (t, 1 H, *J* = 7.0 Hz, H-11), 5.72 (dd, 0.5 H, *J* = 15.6, 7.2 Hz, H-6), 5.73 (dd, 0.5 H, *J* = 15.6, 7.3 Hz, H-6), 5.97 (s, 1 H, H-9), 6.40 (d, 1 H, *J* = 15.6 Hz, H-7), 7.45 (t, 2 H, *J* = 7.9 Hz, H-arom), 7.46 (t, 2 H, *J* = 7.9 Hz, H-arom), 7.57 (t, 1 H, *J* = 7.6 Hz, H-arom), 7.58 (t, 1 H, *J* = 7.4 Hz, H-arom), 8.06 (d, 2 H, *J* = 6.8 Hz, H-arom), 8.08 (d, 2 H, *J* = 6.9 Hz, H-arom).

^{13}C NMR (50 MHz, $CDCl_3$), *four diastereomers*: δ = 13.9 (CH_3-8), 16.5 (CH_3-2), 17.3 (CH_3-10), 28.8 (C-3), 33.4 (C-4), 35.7 (C-2), 61.7 (C-12), 67.9 (C-1), 75.2, 75.8 (C-5), 124.3 (C-12), 126.9 (C-6), 128.3 (C-arom), 129.3 (C-arom), 132.8 (C-arom), 134.0 (C-8 or C-10), 135.2 (C-9), 137.9, 138.0 (C-7), 165.9, 166.4 [O*C*(O)Ph].

IR (film): ν = 3501, 2924, 2854, 1715, 1652, 1602, 1451, 1377, 1315, 1272, 1177, 1113, 1026, 966, 909, 734, 713 cm^{-1}.

MS (DI, CI, NH_3): *m/z* = 480 ($MH^+ + NH_3$), 463 (MH^+), 445 ($MH^+ - H_2O$), 411, 391, 341, 323, 219, 201, 161, 145, 99, 78.

27:

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (d, 3 H, *J* = 6.6 Hz, CH_3-5), 1.21 (qd, 1 H, *J* = 11.2, 3.9 Hz, Hax-4), 1.47 (qd, 1 H, *J* = 11.2, 3.9 Hz, Hb-3), 1.62–1.82 (m, 2 H, Ha-3 + H-5), 1.93–1.96 (m, 1H, Heq-4), 1.91 (s, 3 H, CH_3-3' or CH_3-5'), 1.92 (s, 3 H, CH_3-3' or CH_3-5'), 3.09 (t, 1 H, *J* = 11.2 Hz, Hax-6), 3.82 (dd, 1 H, *J* = 11.2, 6.3 Hz, H-2), 3.93 (ddd, 1 H, *J* = 11.2, 4.3, 2.1 Hz, Heq-6), 4.95 (d, 2 H, *J* = 7.1 Hz, H_2-7'), 5.63 (t, 1 H, *J* = 7.1 Hz, H-6'), 5.71 (dd, 1 H, *J* = 15.8, 6.2 Hz, H-1'), 5.94 (s, 1 H, H-4'), 6.29 (d, 1 H, *J* = 15.8 Hz, H-2'), 7.45 (t, 2 H, *J* = 7.5 Hz, H-arom), 7.57 (t, 1 H, *J* = 8.0 Hz, H-arom), 8.06 (d, 2 H, *J* = 7.2 Hz, H-arom).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7 (CH_3-3'), 17.0 (CH_3-5), 17.3 (CH_3, CH_3-5'), 30.6 (C-5), 32.1 (C-3 or C-4), 32.2 (C-3 or C-4), 61.5 (C-7'), 74.5 (C-6), 77.6 (C-2), 123.8 (C-6'), 128.1 (C-arom), 129.4 (C-arom), 129.9 (C-1'), 130.3 (C-arom), 132.6 (C-arom), 133.9 (C-4'), 134.5 (C-3' or C-5'), 135.1 (C-2'), 135.3 (C-3' or C-5'), 166.1 [O*C*(O)Ph].

IR (film): ν = 2928, 1716, 1602, 1585, 1452, 1375, 1315, 1268, 1176, 1093, 1026, 966, 868, 712 cm^{-1}.

MS (DI, CI, NH_3): *m/z* = 358 ($MH^+ + NH_3$), 341 (MH^+), 313, 287, 269, 236, 219, 201, 165, 161, 121, 99, 78, 61.

Anal. calc. for $C_{22}H_{28}O_3$ (340.5): C, 77.61; H, 8.29; found C, 77.48; H, 8.31.

Ethyl (2*E*,4*S*,7*R/S*,8*E*,10*E*,12*E*)-7,14-Dihydroxy-2,4,10,12-tetramethyltetradeca-2,8,10,12-tetraenoate (2):

To a solution of oxalyl chloride (1.1 mL, 11.9 mmol, 2.0 equiv) in anhyd CH_2Cl_2 (60 mL) at –55 °C was added DMSO (1.9 mL, 23.9 mmol, 4.0 equiv) . This was followed 5 min later with the addition via cannula of a solution of **26** (2.76 g, 5.97 mmol) in anhyd CH_2Cl_2 (20 mL). The resulting slurry was stirred for 1 h and Et_3N (6.9 mL, 49.5 mmol, 8.3 equiv) was added and after 5 min, the mixture was warmed to r.t. The mixture was diluted with CH_2Cl_2 (20 mL) and washed with ice-cold aq 1M HCl (50 mL) and H_2O (50 mL). The aqueous phases were extracted with CH_2Cl_2 (100 mL), the organic layers were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The crude aldehyde (2*S*,5*R/S*,6*E*,8*E*,10*E*,2*S*)-5,12-[bis(benzoyloxy)]-2,8,10-trimethyldodeca-6,8,10-trienal thus obtained was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 1.15 (d, 3 H, *J* = 7.1 Hz, CH_3-2), 1.42–1.58 (m, 2 H, H_2-3), 1.76–1.93 (m, 2 H, H_2-4), 1.91 (s, 3 H, CH_3-8 or CH_3-10), 1.93 (s, 3 H, CH_3-8 or CH_3-10), 2.43–2.38 (m, 1 H, H-2), 4.95 (d, 2 H, *J* = 7.0 Hz, H_2-12), 5.58–5.62 (m, 1 H, H-5), 5.64 (t, 1 H, *J* = 7.0 Hz, H-11), 5.71 (dd, 1 H, *J* = 15.4, 7.2 Hz, H-6), 5.98 (s, 1 H, H-9), 6.40 (d, 1 H, *J* = 15.4 Hz, H-7), 7.43 (t, 2 H, *J* = 7.4 Hz, H-arom), 7.46 (t, 2 H, *J* = 7.7 Hz, H-arom), 7.54–7.58 (m, 2 H, H-arom), 8.05 (d, 2 H, *J* = 6.7 Hz, H-arom), 8.07 (d, 2 H, *J* = 6.4 Hz, H-arom), 9.37 (s, 1 H, H-1).

^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 13.5 (CH_3-2), 14.1 (CH_3-8), 17.6 (CH_3-10), 26.2 (C-3), 32.3 (C-4), 46.0, 46.1 (C-2), 61.7 (C-12), 75.3 (C-5), 124.5 (C-11), 126.5 (C-6), 128.5 (C-arom), 129.7 (C-arom), 133.1 (C-arom), 134.0 (C-8 or C-10), 135.7 (C-9), 138.5 (C-7), 166.0, 166.7 [O*C*(O)Ph], 204.6 (C-1).

IR (film): ν = 2917, 1717, 1653, 1437, 1316, 1269, 1020, 953 cm^{-1}.

MS (DI, CI, NH_3): *m/z* = 478 ($MH^+ + NH_3$), 448, 391, 356, 339, 311, 279, 217, 199, 147, 122, 96, 58.

A solution of the preceding crude aldehyde (2*S*,5*R/S*,6*E*,8*E*,10*E*,2*S*)-5,12-[bis(benzoyloxy)]-2,8,10-trimethyldodeca-6,8,10-trienal (see above) and (ethoxycarbonylethylidene)triphenylphosphorane (4.32 g, 11.9 mmol, 2.0 equiv) in anhyd toluene (40 mL) was warmed at 50 °C for 5 h. Then the toluene was removed under reduced pressure. The residue was dissolved in Et_2O, filtered on a pad of Celite and the solid was washed with Et_2O. The combined filtrate and washings were concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 30:70) gave ethyl (2*E*,4*S*,7*R/S*8*E*,10*E*,12*E*)-7,14-[bis(benzoyloxy)]-2,4,10,12-tetramethyltetradeca-2,8,10,12-tetraenoate (2.63 g, 81% for two steps) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 1.04 (d, 3 H, *J* = 6.5 Hz, CH_3-4), 1.30 (tm, 3 H, *J* = 6.9 Hz, C*H*$_3$CH$_2$O), 1.37–1.58 (m, 2 H, H_2-5), 1.68–1.93 (m, 2 H, H_2-6), 1.85 (d, 1.5 H, *J* = 1.3 Hz, CH_3-2), 1.86 (d, 1.5 H, *J* = 1.3 Hz, CH_3-2), 1.91 (s, 3H, CH_3-10 or CH_3-12), 1.93 (s, 3 H, CH_3-10 or CH_3-12), 2.49–2.58 (m, 1 H, H-4), 4.21 (qm, 2 H, *J* = 6.9 Hz, CH_3C*H*$_2$O), 4.95 (d, 2 H, *J* = 7.0 Hz, H_2-14), 5.52–5.59 (m, 1 H, H-7), 5.64 (t, 1 H, *J* = 7.0 Hz, H-13), 5.69 (dd, 1 H, *J* = 15.6, 7.4 Hz, H-8), 5.97 (s, 1 H, H-11), 6.38 (d, 1 H, *J* = 15.6 Hz, H-9), 6.54 (d, 1 H, *J* = 10.0 Hz, H-3), 7.45 (t, 2 H, *J* = 7.6 Hz, H-arom), 7.47 (t, 2 H, *J* = 7.5 Hz, H-arom), 7.53–7.59 (m, 2 H, H-arom), 8.05 (d, 2 H, *J* = 6.7 Hz, H-arom), 8.07 (d, 2 H, *J* = 6.6 Hz, H-arom).

^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 12.6 (*C*H$_3$CH$_2$O), 14.0 (CH_3-10), 14.3 (CH_3-4), 17.4 (CH_3-12), 17.4 (CH_3-12), 32.4 (C-5 or C-6), 32.8 (C-5 or C-6), 33.1 (C-4), 60.4 (CH$_3$*C*H$_2$O), 61.7 (C-14), 75.4 (C-7), 124.5 (C-13), 127.0 (C-8), 127.2 (C-2), 128.3 (C-arom), 129.6 (C-arom), 132.8 (C-arom), 134.0 (C-10 or C-12), 135.3 (C-11), 138.1 (C-9), 147.3 (C-3), 165.8, 166.4, [O*C*(O)Ph], 168.2 (C-1).

IR (film): ν = 2927, 1716, 1652, 1450, 1366, 1269, 1176, 1107, 1026, 713 cm^{-1}.

MS (DI, CI, NH_3): *m/z* = 562 ($MH^+ + NH_3$), 534, 478, 440, 423, 356, 315, 301, 255, 227, 159, 122, 105, 78.

A solution of ethyl (2*E*,4*S*,7*R/S*8*E*,10*E*,12*E*)-7,14-[bis(benzoyloxy)]-2,4,10,12-tetramethyltetradeca-2,8,10,12-tetraenoate (2.63 g, 4.83 mmol) in NaOEt/EtOH (0.01 M NaOEt in EtOH, 150 mL, 1.50 mmol, 0.3 equiv) was stirred for 24 h at r.t. Then the mixture was extracted with Et_2O and washed with H_2O and brine. The organic layer was dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography on silica gel (Et_2O/petroleum ether, 40:60 to 80:20) gave **2** (1.2 g, 76%) as a colorless oil.

2:

^{1}H NMR (400 MHz, $CDCl_3$), *two diastereomers*: δ = 1.02 (d, 3 H, *J* = 6.7 Hz, CH_3-4), 1.30 (t, 3 H, *J* = 7.2 Hz, C*H*$_3$CH$_2$O), 1.38–1.65 (m, 5 H, H-4 + H_2-5 + 2 OH), 1.64–1.74 (br s, 1 H, OH), 1.82 (s, 3 H, CH_3-10 or CH_3-12), 1.83 (d, 1.5 H, *J* = 1.3 Hz, CH_3-2), 1.84 (d, 1.5 H, *J* = 1.2 Hz, CH_3-2), 1.92 (s, 3 H, CH_3-10 or CH_3-12), 2.47–2.50 (m, 1 H, H-4), 4.12–4.18 (m, 1 H, H-7), 4.19 (q, 2 H, *J* = 7.2 Hz, CH_3C*H*$_2$O), 4.28 (d, 2 H, *J* = 6.8 Hz, H_2-14), 5.58 (t, 1 H, *J* = 6.8 Hz, H-13), 5.70 (dd, 1 H, *J* = 15.6, 7.1 Hz, H-8), 5.90 (s, 1 H, H-11), 6.24 (d, 1 H, *J* = 15.6 Hz, H-9), 6.52 (d, 1 H, *J* = 10.1 Hz, H-3).

^{13}C NMR (50 MHz, $CDCl_3$), *two diastereomers*: δ = 12.6 (*C*H$_3$CH$_2$O), 14.2 (CH_3-10), 14.4 (CH_3-4), 17.2 (CH_3-12), 19.9 (CH_3-2), 32.7, 32.8 (C-5), 33.45, 33.5 (C-4), 35.6 (C-6), 59.6 (C-14), 60.5 (CH$_3$*C*H$_2$O), 75.4, 75.6 (C-7), 127.1 (C-2), 129.7 (C-13), 131.6 (C-8), 133.9 (C-10), 135.0 (C-11), 135.8 (C-12), 136.2 (C-9), 147.4 (C-3), 168.5 (C-1).

IR (film): ν = 3366, 2930, 2868, 1707, 1647, 1448, 1368, 1260, 1188, 1102, 1004, 965, 750 cm^{-1}.
MS (DI, CI, NH_3): *m/z* = 354 ($MH^+ + NH_3$), 336 ($MH^+ + NH_3 - H_2O$), 319, 301, 273, 255, 227, 216, 199, 183, 159, 136, 110, 95.
Anal. calc. for $C_{20}H_{32}0_4$ (336.5): C, 71.39;H, 9.59; found C, 71.35; H, 9.33.

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